Influence of Ring Size in Conformationally Restricted Ring I Analogs of Paromomycin on Antiribosomal and Antibacterial Activity.

General Experimental

All experiments were carried out under a dry argon atmosphere unless otherwise specified. Heating of reaction mixtures was carried out on an aluminum heating block of appropriate size. Chromatographic purifications were carried over silica gel (230-400 mesh). Optical rotations were measured on a digital polarimeter with a path length of 10 cm. NMR spectra were recorded in $CDCl_3$ or D_2O using a 500, 600, or 900 MHz instrument, and assignments were made with the help of COSY, HMBC, and HSQC spectra. High-resolution (HRMS) mass spectra were recorded in the electrospray mode using a Waters TOF mass spectrometer.

1,3,2',2''',6'''-Pentaazido-6,3',6',2'',5'',3''',4'''-hepta-*O*-benzyl-6'-*C*-vinyl-1,3,2',2''',6'''-6'-p-toluenesulfonyloxymethyl-pentadeaminoparomomycin (14(*R*) and 14(*S*)).

To a stirred solution of DMSO (0.22 mL 3.1 mmol) in 1 mL DCM at -78 ^oC under argon was added oxalyl chloride (0.125 mL, 1.46 mmol). After stirring for 10 mins compound **12** (1.00 g, 0.71 mmol) dissolved in DCM (6 mL) was added dropwise. After an additional 45 mins Et_3N (0.45 mL, 3.2 mmol) was added. The reaction mixture was stirred for an additional 2 h then diluted with Et_2O, washed with aqueous NH_4Cl solution, DI water, and brine. The organic layer was concentrated under vacuum to give the intermediate aldehyde as a white foam which was used in the next step without further purification. ESI-HRMS: *m/z* calc for $C_{74}H_{79}N_{15}O_{14}Na$ $[M+Na]^+$ 1424.5829, found 1424.5815. To a stirred solution of aldehyde in THF (14.5 mL) at -78 ^oC was added vinylMgBr solution (2.9 mL, 1 M in THF). After stirring for 45 mins the reaction was quenched with aqueous saturated NH_4Cl solution, diluted with Et_2O, washed with aqueous saturated NH_4Cl solution, brine, dried with Na_2SO_4, and concentrated to give an inseparable mixture of diastereomers which were filtered through silica gel and used in the next step without further purification. ESI-HRMS: *m/z* calc for $C_{74}H_{79}N_{15}O_{14}Na$ $[M+Na]^+$ 1424.5829, found 1424.5815. The above mixture of alcohols was taken up in DMF (4.7 mL), stirred and treated at 0^oC

under argon with NaH (60 % in mineral oil, 0.188 g, 7.78 mmol). After 15 mins TBAI (0.118 g, 0.319 mmol) and BnBr (1.1 mL, 9.3 mmol) were added to the reaction mixture and stirring was continued for 40 mins before quenching with aqueous saturated NH_4Cl solution. The reaction mixture was diluted with Et_2O, washed with aqueous saturated NH_4Cl solution followed by brine, dried with Na_2SO_4, and concentrated. The crude residue was purified over silica gel eluting with hexanes to 80% ethyl acetate in hexanes to give compounds **13** (0.650 g, 0.427 mmol, 60%) as an inseparable mixture of diastereomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.12 (m, 70H, Ar-H), 7.11 – 7.07 (m, 2H, Ar-H), 7.07 – 7.03 (m, 2H, Ar-H), 6.84 – 6.79 (m, 4H, Ar-H), 6.18 – 6.09 (m, 2H, H-1'a, H-7'a), 6.08 (d, *J* = 3.7 Hz, 1H, H-1'b), 5.95 (ddd, *J* = 17.4, 10.3, 8.7 Hz, 1H, H-7'b), 5.64 (d, *J* = 5.7 Hz, 1H, H-1''a), 5.61 (d, *J* = 5.7 Hz, 1H, H-1''b), 5.43 – 5.37 (m, 2H), 5.32 (dd, *J* = 10.3, 1.9 Hz, 1H), 5.10 (dd, *J* = 17.3, 1.9 Hz, 1H), 4.97 (d, *J* = 10.7 Hz, 1H), 4.94 (d, *J* = 10.7 Hz, 1H), 4.88 – 4.75 (m, 5H), 4.75 – 4.71 (m, 2H), 4.71 – 4.51 (m, 10H), 4.50 – 4.44 (m, 4H), 4.44 – 4.38 (m, 4H), 4.35 – 4.24 (m, 9H), 4.23 – 4.20 (m, 2H), 4.14 – 4.03 (m, 5H), 3.98 – 3.95 (m, 1H), 3.94 – 3.88 (m, 3H), 3.85 – 3.81 (m, 2H), 3.80 (s, 3H), 3.79 – 3.71 (m, 9H), 3.65 (dd, *J* = 12.9, 8.5 Hz, 1H), 3.63 – 3.51 (m, 4H), 3.50 – 3.37 (m, 4H), 3.35 (t, *J* = 2.5 Hz, 1H), 3.33 (t, *J* = 2.5 Hz, 1H), 3.26 (t, *J* = 9.2 Hz, 1H), 3.24 – 3.19 (m, 2H), 3.17 (dd, *J* = 10.4, 3.7 Hz, 1H), 3.13 (t, *J* = 2.7 Hz, 1H), 3.12 (t, *J* = 2.3 Hz, 1H), 2.97 – 2.93 (m, 2H), 2.89 (dd, *J* = 13.0, 4.0 Hz, 1H), 2.23 – 2.17 (m, 2H, H-2eqa, H-2eqb), 1.35 – 1.23 (m, 2H, H-2axa, H-2axb). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.09, 159.04, 138.7, 138.4, 138.3, 138.1, 138.0, 137.9, 137.62, 137.61, 137.1, 137.04, 137.00, 136.97 (Ar), 136.2 (C-7'a), 134.0 (C-7'b), 130.7, 130.5, 128.93, 128.88, 128.67, 128.66, 128.49, 128.48, 128.41, 128.38, 128.35, 128.32, 128.31, 128.25, 128.19, 128.17, 128.14, 128.11, 128.07, 128.03, 127.9, 127.83, 127.82, 127.78, 127.74, 127.72, 127.65, 127.61, 127.48, 127.45, 127.40, 127.37, 127.31, 120.26, 118.7, 113.74, 113.70 (Ar), 106.1 (C-1''a), 105.9 (C-1''b), 98.7 (C-1'''b), 98.6 (C-1'''a), 96.0 (C-1'b), 95.7 (C-1'b), 84.12, 84.05, 82.4, 82.1, 82.0, 81.93, 81.87, 81.6, 80.70, 80.67, 79.4, 78.2, 77.8, 77.7, 75.60, 75.59, 75.4, 74.99, 74.97, 74.8, 74.4, 74.3, 74.13, 74.07, 73.86, 73.84, 73.29, 73.28, 73.19, 73.1, 73.01, 72.95, 72.90, 72.39, 72.37, 71.8, 71.7, 71.5, 70.5, 70.3, 70.2,

69.8, 63.3, 63.2, 60.40, 60.39, 60.0, 59.7, 57.4, 57.3, 55.3, 55.2, 51.1, 50.9, 32.5 (C-2). ESI-HRMS: *m/z* calc for $C_{82}H_{87}N_{15}O_{15}Na$ $[M+Na]^+$ 1544.6404, found 1544.6403. Ozone gas was bubbled through a solution of mixture **13** (0.650 g, 0.427 mmol) in DCM/MeOH (4:1, 23.2 mL) at -78 ^oC. After 0.5 h the solution turned pale blue and the reaction mixture was sparged with argon followed by addition of $NaBH_4$ (59 mg, 1.6 mmol). After 1 h the reaction was quenched with acetone and concentrated under vacuum. The crude residue was dissolved in Et_2O, washed with NH_4Cl solution followed by brine, dried with Na_2SO_4, and concentrated to give the alcohols as an inseparable mixture of diastereomers which were used without further purification. To a stirred solution of the 7'-alcohols in pyridine (4.1 mL) was added TsCl (0.120 g, 0.629 mmol). After 19 h further TsCl (0.022 g, 0.115 mmol) and DMAP (5.9 mg 0.05 mmol) were added. After stirring for an additional 5 h the reaction mixture was diluted with Et_2O, washed with 1 N HCl, saturated aqueous $NaHCO_3$ solution, and brine. The organic layer was dried with Na_2SO_4 and concentrated to give the tosylates as an inseparable mixture of diastereomers which were used in the next step without further purification. TFA (0.89 mL) was added to a stirred solution of tosylates in DCM (8 mL) at 0^oC. After 0.5h the reaction mixture was diluted with Et_2O and washed with DI water, aqueous saturated $NaHCO_3$ solution, and brine. The organic layer was dried with Na_2SO_4, concentrated, and purified over silica gel to give compounds **14(*R*)** and **14(*S*)** as a mixture of diastereomers (0.367 g, 0.235 mmol, 55%). The mixture of diastereomers was then purified using silica gel HPLC to give **14(*R*)** (91.5 mg 0.059 mmol) in 14% isolated yield and **14(*S*)** (95.2 mg, 0.061 mmol) in 14% isolated yield. **14(*R*)** $[\alpha]_D^{23}$ = 60.3 (*c* = 1.0, $CHCl_3$), ^1H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H, ArH), 7.40 – 7.13 (m, 37H, ArH), 6.11 (d, *J* = 3.5 Hz, 1H, H-1'), 5.68 (d, *J* = 6.1 Hz, 1H, H-1''), 4.97 (d, *J* = 10.7 Hz, 1H, $PhCH_2O$), 4.95 (d, *J* = 1.9 Hz, 1H, H-1'''), 4.83 (d, *J* = 11.2 Hz, 1H, $PhCH_2O$), 4.78 (d, *J* = 11.2 Hz, 1H, $PhCH_2O$), 4.70 (d, *J* = 10.6 Hz, 1H, $PhCH_2O$), 4.66 – 4.60 (m, 2H, $PhCH_2O$), 4.53 – 4.49 (m, 2H, $PhCH_2O$), 4.47 – 4.40 (m, 4H, $PhCH_2O$), 4.31 (d, *J* = 12.0 Hz, 1H, $PhCH_2O$), 4.30 – 4.27 (m, 3H, H-7', H-3'', H-4''), 4.24 (d, *J* = 12.1 Hz, 1H, $PhCH_2O$), 4.21 (dd, *J* = 11.1, 2.6 Hz, 1H, H-7'), 4.09 (dd, *J* = 9.7, 5.2 Hz, 1H, H-5'), 3.95 (dd, *J* = 6.1, 4.8 Hz, 1H, H-2''),

3.90 (m, 2H, H-5, H-3'), 3.80 (m, 2H, H-5'', H-5'), 3.76 (t, *J* = 2.8 Hz, 1H, H-3'''), 3.73 – 3.64 (m, 3H, H-4, H-6', H-6'''), 3.55 (dd, *J* = 10.4, 2.8 Hz, 1H, H-5''), 3.45 – 3.29 (m, 5H, H-1, H-3, H-6, H-4', H-2'''), 3.11 (t, *J* = 2.4 Hz, 1H, H-4'''), 2.85 (dd, *J* = 13.0, 3.7 Hz, 1H, H-6'''), 2.80 (dd, *J* = 10.4, 3.5 Hz, 1H, H-2'), 2.41 (s, 3H, Ar-CH_3), 2.14 (dt, *J* = 13.2, 4.6 Hz, 1H, H-2eq), 1.37 (q, *J* = 12.7 Hz, 1H, H-2ax). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 138.3, 138.2, 138.1, 137.7, 137.0, 136.95, 136.91, 133.1, 133.0, 129.9, 128.7, 128.6, 128.52, 128.50, 128.42, 128.35, 128.32, 128.28, 128.21, 128.18, 128.15, 128.11, 127.90, 127.86, 127.81, 127.75, 127.4, 127.1 (Ar), 106.0 (C-1''), 98.7 (C-1'''), 95.4 (C-1'), 84.1 (C-6), 82.6 (C-2''), 82.1 (C-4''), 81.9 (C-5), 79.3 (C-3'), 78.6 (C-6'), 75.5 (C-3''), 75.2 ($PhCH_2O$), 75.0 ($PhCH_2O$), 74.4 (C-5'''), 74.2 (C-4), 73.2 (C-4'), 73.1 ($PhCH_2O$), 72.8 (C-3'''), 72.3 ($PhCH_2O$), 72.2 ($PhCH_2O$), 71.7 ($PhCH_2O$), 71.5 (C-4'''), 70.2 (C-5''), 69.3 (C-5'), 67.9 (C-7'), 62.2 (C-2'), 60.45 (C-1), 60.41 (C-3), 57.2 (C-2'''), 51.1 (C-6'''), 32.2 (C-2), 21.6 (OTs-CH_3). ESI-HRMS: *m/z* calc for $C_{80}H_{85}N_{15}O_{17}SNa$ $[M+Na]^+$ 1582.5866, found 1582.5872. **14(*S*)** $[\alpha]_D^{23}$ = 58.7 (*c* = 1.0, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H, ArH), 7.39 – 7.11 (m, 37H, ArH), 6.15 (d, *J* = 3.6 Hz, 1H, H-1'), 5.65 (d, *J* = 6.0 Hz, 1H, H-1''), 4.97 (d, *J* = 10.7 Hz, 1H, $PhCH_2O$-), 4.89 – 4.86 (m, 2H, H-1''', $PhCH_2O$-), 4.70 (d, *J* = 10.6 Hz, 1H, $PhCH_2O$-), 4.66 – 4.58 (m, 4H, $PhCH_2O$-), 4.54 – 4.47 (m, 3H, $PhCH_2O$-), 4.42 – 4.37 (m, 2H, $PhCH_2O$-), 4.34 (dd, *J* = 9.9, 6.2 Hz, 1H, H-7'), 4.30 (d, *J* = 12.0 Hz, 1H, $PhCH_2O$-), 4.26 – 4.22 (m, 2H, H-4'', $PhCH_2O$-), 4.20 (dd, *J* = 5.0, 2.5 Hz, 1H, H-3''), 4.10 (dd, *J* = 10.0, 6.5 Hz, 1H, H-7'), 3.99 (dd, *J* = 9.9, 2.3 Hz, 1H, H-5'), 3.93 – 3.90 (m, 2H, H-5, H-6'), 3.88 (dd, *J* = 4.8, 1.2 Hz, 1H, H-2''), 3.86 (d, *J* = 9.6 Hz, 1H, H-3'), 3.76 – 3.71 (m, 3H, H-5'', H-3''', H-5'''), 3.62 (t, *J* = 9.4 Hz, 1H, H-4), 3.59 – 3.51 (m, 3H, H-4', H-5'', H-6'''), 3.48 – 3.37 (m, 2H, H-1, H-3), 3.35 (t, *J* = 9.3 Hz, 1H, H-6), 3.32 (t, *J* = 2.4 Hz, 1H, H-2'''), 3.11 (t, *J* = 2.5 Hz, 1H, H-4'''), 2.93 (dd, *J* = 10.3, 3.6 Hz, 1H, H-2'), 2.90 (dd, *J* = 12.9, 4.3 Hz, 1H, H-6'''), 2.43 (s, 3H, Ar-CH_3), 2.17 (dt, *J* = 13.2, 4.6 Hz, 1H, H-2eq), 1.51 (q, *J* = 12.7 Hz, 1H, H-2ax). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.9, 138.2, 138.0, 137.6, 137.5, 137.04, 136.98, 129.9, 128.7, 128.6, 128.47, 128.45, 128.43, 128.39, 128.33, 128.29, 128.22, 128.14, 128.09, 127.96, 127.91, 127.80, 127.78, 127.73, 127.43, 127.40 (Ar), 105.9 (C-1''), 98.7 (C-1'''), 96.0 (C-1'), 84.0 (C-6), 82.2 (C-2''), 81.9

(C-4''), 81.7 (C-5), 79.9 (C-3'), 75.5 (C-3''), 75.1 ($PhCH_2O$), 75.0 ($PhCH_2O$), 74.4 (C-4), 74.2 (C-3'''), 74.0 ($PhCH_2O$), 73.6 (C-6'), 73.23 ($PhCH_2O$), 73.17 ($PhCH_2O$), 72.9 (C-5'''), 72.3 ($PhCH_2O$), 71.7 ($PhCH_2O$), 71.4 (C-4'''), 70.3 (C-5'), 69.9 (C-5''), 69.7 (C-4'), 68.6 (C-7'), 62.5 (C-2'), 60.5 (C-1), 60.4 (C-3), 57.2 (C-2'''), 50.9 (C-6'''), 32.2 (C-2), 21.7 (Ar-CH_3). ESI-HRMS: *m/z* calc for $C_{80}H_{85}N_{15}O_{17}SNa$ $[M+Na]^+$ 1582.5866, found 1582.5854.

4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (15(ax)).

To a stirred solution of compound **14(*R*)** (41.8 mg, 0.027 mmol) in DMF (1.1 mL) was added NaH (60% in mineral oil, 2.2 mg, 0.055 mmol). The reaction mixture was stirred for 1 h, then quenched with aqueous saturated NH_4Cl solution, diluted with Et_2O, washed with brine, dried with Na_2SO_4, and concentrated under vacuum. The crude residue was purified using silica gel column chromatography (20 % EtOAc in hexanes) to obtain compound **15(ax)** (19.5 mg, 0.014 mmol) as a white foam in 52% yield. $[\alpha]_D^{23}$ = 72.0 (*c* = 1.0, $CHCl_3$), ^{1}H NMR (600 MHz, C_6D_6) δ 7.54 – 7.46 (m, 4H, ArH), 7.33 – 7.29 (m, 2H, ArH), 7.28 – 7.22 (m, 4H, ArH), 7.18 – 6.94 (m, 25H, ArH), 6.46 (d, *J* = 3.8 Hz, 1H, H-1'), 5.98 (d, *J* = 5.4 Hz, 1H, H-1''), 5.14 (d, *J* = 11.7 Hz, 1H, $PhCH_2O$), 4.99 (d, *J* = 2.1 Hz, 1H, H-1'''), 4.97 (d, *J* = 10.6 Hz, 1H, $PhCH_2O$), 4.89 (d, *J* = 11.7 Hz, 1H, $PhCH_2O$), 4.74 (d, *J* = 12.0 Hz, 1H, $PhCH_2O$), 4.61 (d, *J* = 10.5 Hz, 1H, $PhCH_2O$), 4.57 (q, *J* = 2.9 Hz, 1H, H-4''), 4.49 (dd, *J* = 4.9, 2.8 Hz, 1H, H-3''), 4.41 – 4.35 (m, 5H, $PhCH_2O$), 4.34 (d, *J* = 9.4 Hz, 1H, $PhCH_2O$), 4.30 (d, *J* = 11.8 Hz, 1H, $PhCH_2O$), 4.25 (d, *J* = 11.9 Hz, 1H, $PhCH_2O$), 4.21 (dd, *J* = 10.3, 4.3 Hz, 1H, H-5'), 4.12 (t, *J* = 5.2 Hz, 1H, H-2''), 4.11 – 4.05 (m, 2H, H-4', $PhCH_2O$), 4.00 – 3.88 (m, 5H, H-6', H-7', $PhCH_2O$), 3.86 (dd, *J* = 10.5, 2.5 Hz, 1H, H-5''), 3.81 (t, *J* = 8.9 Hz, 1H, H-5), 3.73 (ddd, *J* = 8.3, 4.6, 2.1 Hz, 1H, H-5'''), 3.69 – 3.64 (m, 2H, H-4, H-3'''), 3.56 (dd, *J* = 10.5, 3.2 Hz, 1H, H-5''), 3.39 (dd, *J* = 12.8, 8.2 Hz, 1H, H-6'''), 3.34 (t, *J* = 2.7 Hz, 1H, H-2'''), 3.18 (dd, *J* = 9.9, 3.9 Hz, 1H, H-2'), 2.97 – 2.95 (m, 1H, H-4'''), 2.88 (t, *J* = 9.4 Hz, 1H, H-6), 2.75 (dd, *J* = 12.9, 4.6 Hz, 1H, H-6'''), 2.71 (ddd, *J* = 12.8, 9.6, 4.6 Hz, 1H, H-3),

2.57 (ddd, *J* = 12.4, 9.6, 4.5 Hz, 1H, H-1), 1.41 (dt, *J* = 12.9, 4.6 Hz, 1H, H-2eq), 0.88 (q, *J* = 12.7 Hz, 1H, H-2ax). ^{13}C NMR (151 MHz, C_6D_6) δ 138.6, 138.4, 138.3, 138.0, 137.4, 137.3, 128.4, 128.35, 128.26, 128.22, 128.19, 128.00, 127.98, 127.94, 127.89, 127.6, 127.41, 127.37, 127.35 (Ar), 106.3 (C-1''), 98.8 (C-1', C-1'''), 83.9 (C-6), 82.4 (C-4''), 82.4 (C-2''), 81.6 (C-5), 79.3 (C-4'), 78.0 (C-3'), 75.9 (C-3''), 75.6 (C-4), 75.3 (C-6'), 75.0 ($PhCH_2O$), 74.1 (C-5', C-7', C-5'''), 73.6 (C-3'''), 73.1 ($PhCH_2O$), 73.0 ($PhCH_2O$), 72.7 ($PhCH_2O$), 72.4 (C-4'''), 72.2 ($PhCH_2O$), 71.9 ($PhCH_2O$), 71.6 ($PhCH_2O$), 70.0 (C-5''), 62.5 (C-2'), 59.9 (C-1), 59.8 (C-3), 56.8 (C-2'''), 50.9 (C-6'''), 31.8 (C-2). ESI-HRMS: *m/z* calc for $C_{73}H_{77}N_{15}O_{14}Na$ $[M+Na]^+$ 1410.5672, found 1410.5699.

4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (7).

To a solution of compound **15(ax)** (19.5 mg, 0.014 mmol) in 1:1 1,4-dioxane/10% aqueous AcOH (0.6 mL) was added Pd/C (10 wt%, 40.6 mg). The reaction mixture was stirred under 50 psi H_2 for 30 h before filtration through Celite and concentration. The crude residue was purified using CM Sephadex ion exchange column chromatography (0.1-0.8% aqueous NH_4OH) followed by lyophilization with acetic acid to give the pentaacetate salt **7** (5.9 mg, 0.0064 mmol) in 46% yield as a white powder. $[\alpha]_D^{23}$ = 38.6 (*c* = 0.2, water) ^{1}H NMR (600 MHz, D_2O) δ 5.67 (d, *J* = 4.2 Hz, 1H, H-1'), 5.22 (d, *J* = 1.9 Hz, 1H, H-1''), 5.11 (d, *J* = 1.8 Hz, 1H, H-1'''), 4.37 (dd, *J* = 7.2, 4.8 Hz, 1H, H-3''), 4.33 (t, *J* = 4.5 Hz, 1H, H-6'), 4.25 (dd, *J* = 4.9, 2.0 Hz, 1H, H-2''), 4.19 – 4.12 (m, 2H, H-7', H-5'''), 4.06 – 4.02 (m, 2H, H-4'', H-3'''), 3.91 (t, *J* = 9.9 Hz, 1H, H-3'), 3.77 – 3.70 (m, 3H, H-5', H-7', H-5''), 3.67 (t, *J* = 9.1 Hz, 1H, H-5), 3.65 – 3.63 (m, 1H, H-4'''), 3.62 – 3.56 (m, 2H, H-4, H-5''), 3.51 (t, *J* = 9.9 Hz, 1H, H-4'), 3.44 (t, *J* = 9.8 Hz, 1H, H-6), 3.40 – 3.37 (m, 1H, H-2'''), 3.25 (dd, *J* = 13.6, 6.8 Hz, 1H, H-6'''), 3.19 (dd, *J* = 13.6, 3.8 Hz, 1H, H-6'''), 3.13 (dd, *J* = 10.2, 4.2 Hz, 1H, H-2'), 3.10 – 3.05 (m, 1H, H-1), 3.04 – 2.98 (m, 1H, H-3), 2.12 (dt, *J* = 12.9, 4.4 Hz, 1H, H-2eq), 1.73 (d, *J* = 1.1 Hz, 15H, AcOH), 1.44 (q, *J* = 12.6 Hz, 1H, H-2ax). ^{13}C NMR (151 MHz, D_2O) δ 181.3 (AcOH), 110.0 (C-1''), 98.3 (C-1'), 95.3 (C-1'''), 85.1 (C-5), 81.0 (C-4''), 79.3 (C-6), 77.0 (C-4'), 76.0 (C-4'), 74.8 (C-7'), 73.3

(C-3''), 73.2 (C-2''), 73.0 (C-4), 70.2 (C-5'), 69.9 (C-5'''), 67.7 (C-3'), 67.6 (C-3'''), 67.3 (C-6'), 59.8 (C-4'''), 54.6 (C-5''), 50.9 (C-2'), 50.2 (C-2'''), 48.5 (C-1), 40.3 (C-3), 30.7 (C-2), 23.2 (AcOH). ESI-HRMS: *m/z* calc for $C_{24}H_{46}N_5O_{14}$ $[M+H]^+$ 628.3041, found 628.3060.

4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,7-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (15(eq)).

To a stirred solution of compound **14(*S*)** (39.8 mg, 0.026 mmol) in DMF (1.0 mL) was added NaH (60% in mineral oil, 2.5 mg, 0.062 mmol). After stirring for 3 h the reaction was not complete and NaH (2.5 mg, 0.062 mmol) was added. After an additional 30 mins the reaction was quenched with aqueous saturated NH_4Cl solution, diluted with Et_2O, washed with brine, dried with Na_2SO_4, and concentrated under vacuum. The crude residue was purified using silica gel column chromatography (20 % EtOAc in hexanes) to obtain compound **15(eq)** (24.4 mg, 0.018 mmol) as a white foam in 69% yield. $[\alpha]_D^{23}$ = 76.4 (*c* = 1.0, $CHCl_3$) ^{1}H NMR (600 MHz, C_6D_6) δ 7.52 – 7.45 (m, 4H, ArH), 7.36 – 7.26 (m, 6H, ArH), 7.21 – 6.95 (m, 25H, ArH), 6.57 (d, *J* = 3.9 Hz, 1H, H-1'), 5.99 (d, *J* = 5.6 Hz, 1H, H-1''), 5.08 (d, *J* = 11.6 Hz, 1H, $PhCH_2O$), 5.02 (d, *J* = 1.8 Hz, 1H, H-1'''), 4.93 (d, *J* = 10.5 Hz, 1H, $PhCH_2O$), 4.87 (d, *J* = 11.6 Hz, 1H, $PhCH_2O$), 4.68 (d, *J* = 11.6 Hz, 1H, $PhCH_2O$), 4.58 – 4.55 (m, 2H, H-4'', $PhCH_2O$), 4.54 – 4.45 (m, 3H, H-3', H-5', H-3''), 4.41 – 4.36 (m, 2H, $PhCH_2O$), 4.36 – 4.32 (m, 2H, $PhCH_2O$), 4.31 – 4.26 (m, 2H, $PhCH_2O$), 4.13 (t, *J* = 5.2 Hz, 1H, H-2''), 4.06 (d, *J* = 11.8 Hz, 1H, $PhCH_2O$), 4.02 (td, *J* = 7.6, 5.3 Hz, 1H, H-6'), 3.99 – 3.95 (m, 2H, $PhCH_2O$), 3.94 – 3.89 (m, 2H, H-7', H-5''), 3.85 – 3.80 (m, 2H, H-4, H-7'), 3.77 – 3.70 (m, 2H, H-5, H-5'''), 3.66 (t, *J* = 3.0 Hz, 1H, H-3'''), 3.57 (dd, *J* = 10.5, 2.8 Hz, 1H, H-5''), 3.42 (dd, *J* = 12.8, 8.4 Hz, 1H, H-6'''), 3.36 – 3.33 (m, 1H, H-2'''), 3.26 (t, *J* = 9.7 Hz, 1H, H-4'), 3.09 (dd, *J* = 9.8, 3.9 Hz, 1H, H-2'), 2.96 – 2.93 (m, 1H, H-4'''), 2.86 (t, *J* = 9.4 Hz, 1H, H-6), 2.78 (ddd, *J* = 12.7, 9.8, 4.6 Hz, 1H, H-3), 2.71 (dd, *J* = 12.8, 4.2 Hz, 1H, H-6'''), 2.56 (ddd, *J* = 12.5, 9.9, 4.4 Hz, 1H, H-1), 1.38 (dt, *J* = 12.7, 4.4 Hz, 1H, H-2eq), 0.86 (q, *J* = 12.7 Hz, 1H, H-2ax). ^{13}C NMR (151 MHz, C_6D_6) δ 138.6, 138.4, 138.34, 138.27, 138.0, 137.4, 137.3, 128.43, 128.35, 128.27,

128.22, 128.1, 128.00, 127.96, 127.94, 127.6, 127.31, 127.28 (Ar), 106.4 (C-1''), 98.8 (C-1'''), 98.3 (C-1'), 84.1 (C-6), 82.6 (C-2''), 82.4 (C-4''), 82.0 (C-4), 81.8 (C-4'), 78.9 (C-6'), 77.1 (C-5'), 77.0 (C-3'), 75.9 (C-3''), 75.7 (C-5), 75.0 ($PhCH_2O$), 74.2 (C-5'''), 73.5 (C-3'''), 73.3 ($PhCH_2O$), 73.1 ($PhCH_2O$), 72.8 ($PhCH_2O$), 72.3 (C-7'), 72.2 (C-4'''), 71.8 ($PhCH_2O$), 71.6 ($PhCH_2O$), 70.3 (C-5''), 62.7 (C-2'), 60.0 (C-1), 59.9 (C-3), 56.7 (C-2'''), 51.0 (C-6'''), 32.0 (C-2). ESI-HRMS: *m/z* calc for $C_{73}H_{77}N_{15}O_{14}Na$ $[M+Na]^+$ 1410.5672, found 1410.5570.

4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (6).

To a solution of compound **15(eq)** (24.4 mg, 0.018 mmol) in 1:1 1,4-dioxane/10% aqueous AcOH (0.6 mL) was added Pd/C (10 wt%, 47.8 mg). The reaction mixture was stirred under 50 psi H_2 for 30 h before filtration through Celite and concentration. The crude residue was purified using CM Sephadex ion exchange column chromatography (0.1-0.6% aqueous NH_4OH) followed by lyophilization with acetic acid to give the pentaacetate salt **6** (3.1 mg, 0.0033 mmol) in 18% yield as a white powder. $[\alpha]_D^{23}$ = 54.6 (*c* = 0.1, water) ^{1}H NMR (600 MHz, D_2O) δ 5.58 (d, *J* = 4.3 Hz, 1H, H-1'), 5.23 (d, *J* = 2.1 Hz, 1H, H-1''), 5.11 (d, *J* = 1.8 Hz, 1H, H-1'''), 4.42 (td, *J* = 8.0, 5.5 Hz, 1H, H-6'), 4.38 (dd, *J* = 7.0, 4.8 Hz, 1H, H-3''), 4.24 (dd, *J* = 4.9, 2.1 Hz, 1H, H-2''), 4.16 – 4.12 (m, 2H, H-7', H-5'''), 4.07 – 4.02 (m, 2H, H-4'', H-3'''), 3.94 (t, *J* = 9.8 Hz, 1H, H-3'), 3.83 (dd, *J* = 10.1, 7.9 Hz, 1H, H-5'), 3.75 (dd, *J* = 12.4, 3.1 Hz, 1H, H-5''), 3.68 (t, *J* = 9.2 Hz, 1H, H-5), 3.66 – 3.64 (m, 1H, H-4'''), 3.64 – 3.58 (m, 2H, H-7', H-5''), 3.56 (t, *J* = 9.4 Hz, 1H, H-4), 3.43 (t, *J* = 9.8 Hz, 1H, H-6), 3.39 – 3.34 (m, 2H, H-4', H-2'''), 3.26 (dd, *J* = 13.6, 6.8 Hz, 1H, H-6'''), 3.20 (dd, *J* = 13.6, 3.9 Hz, 1H, H-6'''), 3.10 – 3.03 (m, 2H, H-1, H-2'), 3.02 – 2.96 (m, 1H, H-3), 2.11 (dt, *J* = 12.9, 4.3 Hz, 1H, H-2eq), 1.75 (s, 13H, AcOH), 1.41 (q, *J* = 12.6 Hz, 1H, H-2ax). ^{13}C NMR (151 MHz, D_2O) δ 181.3 (AcOH), 109.8 (C-1''), 98.6 (C-1'), 95.6 (C-1'''), 84.9 (C-5), 81.1 (C-4''), 80.4 (C-4), 78.8 (C-4'), 77.1 (C-5'), 75.0 (C-3''), 73.5 (C-6), 73.4 (C-2''), 73.0 (C-7'), 70.8 (C-6'), 70.3 (C-5'''), 69.7 (C-3'), 67.9 (C-3'''), 67.4 (C-4'''), 59.9

(C-5’’), 54.7 (C-2’), 51.0 (C-2’’’), 50.3 (C-1), 48.8 (C-3), 40.4 (C-6’’’), 31.2 (C-2), 23.2 (AcOH). ESI-HRMS: *m/z* calc for $C_{24}H_{46}N_5O_{14}$ $[M+H]^+$ 628.3041, found 628.3038.

4’-*O*-Allyl-1,3,2’,2’’’,6’’’-Pentaazido-6,3’,2’’,5’’,3’’’,4’’’-hexa-*O*-benzyl-6’-*O*-triisopropylsilyl-1,3,2’,2’’’,6’’’-pentadeaminoparomomycin (17).

A stirred solution of compound **16** (2.51 g 1.73 mmol) in DMF (34 mL) was treated with NaH (0.140 g, 3.50 mmol) and stirred for 20 mins. TBAI (0.200 g, 0.541 mmol) and allyl bromide (0.30 mL, 3.5 mmol) were added and stirring was continued. After 3 h the reaction was quenched with aqueous saturated NH_4Cl solution, diluted with Et_2O, washed with DI water and brine, dried with Na_2SO_4, and concentrated. The crude residue was purified using silica gel column chromatography (10% EtOAc in hexanes) to give compound **17** (1.94 g, 1.31 mmol) as a white foam in 76% yield. $[\alpha]_D^{23}$ = 68.8 (*c* = 1.0, DCM), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H, ArH), 7.36 – 7.23 (m, 18H, ArH), 7.22 – 7.14 (m, 10H, ArH), 6.10 (d, *J* = 3.7 Hz, 1H, H-1’), 5.91 (ddt, *J* = 17.3, 10.7, 5.5 Hz, 1H, -CH_2-CH=CH_2), 5.65 (d, *J* = 5.9 Hz, 1H, H-1’’), 5.25 (dq, *J* = 17.2, 1.7 Hz, 1H, -CH_2-CH=CH_2), 5.14 (dq, *J* = 10.4, 1.5 Hz, 1H, -CH_2-CH=CH_2), 4.94 (d, *J* = 10.7 Hz, 1H, $PhCH_2O$), 4.87 (d, *J* = 1.9 Hz, 1H, H-1’’’), 4.83 (d, *J* = 10.7 Hz, 1H, $PhCH_2O$), 4.80 (d, *J* = 10.7 Hz, 1H, $PhCH_2O$), 4.67 (d, *J* = 10.7 Hz, 1H, $PhCH_2O$), 4.613 (d, *J* = 11.9, 1H, $PhCH_2O$), 4.610 (d, *J* = 12.1, 1H, $PhCH_2O$), 4.55 (d, *J* = 12.0 Hz, 1H, $PhCH_2O$), 4.46 (d, *J* = 11.7 Hz, 1H, $PhCH_2O$), 4.409 (d, *J* = 12.0, 1H, $PhCH_2O$), 4.403 (d, *J* = 12.0, 1H, $PhCH_2O$), 4.33 – 4.21 (m, 5H, H-3’’, H-4’’, -CH_2-CH=CH_2, $PhCH_2O$), 4.13 (ddt, *J* = 12.7, 5.6, 1.5 Hz, 1H, -CH_2-CH=CH_2), 4.03 (dd, *J* = 10.4, 9.0 Hz, 1H, H-3’), 3.98 – 3.91 (m, 4H, H-5, H-5’, H-6’, H-2’’), 3.84 (dd, *J* = 5.5, 11.1 Hz, 1H, H-6’), 3.76 – 3.71 (m, 4H, H-4, H-5’’, H-3’’’, H-5’’’), 3.59 (dd, *J* = 12.9, 8.4 Hz, 1H, H-6’’’), 3.54 (dd, *J* = 10.4, 3.3 Hz, 1H, H-5’’), 3.45 (ddd, *J* = 12.4, 9.7, 4.6 Hz, 1H, H-3), 3.45 (ddd, *J* = 12.4, 9.7, 4.6 Hz, 1H, H-1), 3.34 – 3.31 (m, 1H, H-2’’’), 3.28 (t, *J* = 9.3 Hz, 1H, H-4’), 3.25 (t, *J* = 9.4 Hz, 1H, H-6), 3.12 – 3.10 (m, 1H, H-4’’’), 3.04 (dd, *J* = 10.4, 3.7 Hz, 1H, H-2’), 2.89 (dd, *J* = 12.9, 4.2 Hz, 1H, H-6’’’), 2.22 (dt, *J* = 13.1, 4.6 Hz, 1H, H-2eq), 1.36 (q, *J* = 12.7 Hz, 1H, H-2ax), 1.17 – 1.06 (m, 21H, OTIPS). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.3, 138.1, 137.9, 137.7, 137.07, 136.93 (Ar), 134.9 (-

CH_2-CH=CH_2), 128.7, 128.5, 128.41, 128.38, 128.35, 128.32, 128.31, 128.28, 128.23, 128.16, 127.82, 127.76, 127.73, 127.48, 127.46, 127.42 (Ar), 116.5 (-CH_2-CH=CH_2), 105.9 (C-1''), 98.6 (C-1'''), 95.6 (C-1'), 84.2 (C-6), 82.6 (C-2''), 82.0 (C-4''), 81.7 (C-5), 80.1 (C-3'), 78.1 (C-4'), 75.6 (C-3''), 75.4 (PhCH_2O), 75.0 (PhCH_2O), 74.5 (C-4), 74.2 (C-5'''), 73.5 (-CH_2-CH=CH_2), 73.3 (PhCH_2O), 73.2 (PhCH_2O), 72.9 (C-3'''), 72.7 (C-5'), 72.4 (PhCH_2O), 71.7 (PhCH_2O), 71.4 (C-4'''), 69.9 (C-5''), 63.4 (C-2'), 62.9 (C-6'), 60.4 (C-1), 60.0 (C-3), 57.3 (C-2'''), 51.0 (C-6'''), 32.6 (C-2), 18.1 (^{i}Pr-CH_3), 18.1 (^{i}Pr-CH_3), 12.0 (^{i}Pr-CH-). ESI-HRMS: *m/z* calc for $C_{77}H_{95}N_{15}O_{14}SiNa$ $[M+Na]^+$ 1504.6856, found 1504.6855.

4'-*O*-Allyl-1,3,2',2''',6'''-Pentaazido-6,3',2'',5'',3''',4'''-hexa-*O*-benzyl-1,3,2',2''',6'''-pentadeaminoparomomycin (18).

To a stirred solution of **17** (2.60 g, 1.75 mmol) in THF (33 mL) was added TBAF solution (1 M in THF, 10.5 mL). The reaction mixture was stirred under argon for 1 h with monitoring by TLC. After completion, the reaction mixture was concentrated under vacuum and the residue was dissolved in ethyl acetate and washed with saturated aqueous $NaHCO_3$ followed by brine. The organic layer was dried with Na_2SO_4, filtered, and concentrated under vacuum. Purification using silica gel column chromatography (15-30% EtOAc in hexanes) gave the product **18** (2.03 g, 1.53 mmol) in 87% yield as a white foam. $[\alpha]_D^{23}$ = 85.2 (*c* = 1.0, DCM), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H, ArH), 7.36 – 7.24 (m, 19H, ArH), 7.22 – 7.13 (m, 9H, ArH), 6.13 (d, *J* = 3.7 Hz, 1H, H-1'), 5.89 (ddt, *J* = 17.2, 10.8, 5.5 Hz, 1H, -CH_2-**CH**=CH_2), 5.68 (d, *J* = 5.7 Hz, 1H, H-1''), 5.25 (dq, *J* = 17.2, 1.7 Hz, 1H, -CH_2-CH=**CH_2**), 5.14 (dq, *J* = 10.5, 1.4 Hz, 1H, -CH_2-CH=**CH_2**), 4.98 (d, *J* = 10.6 Hz, 1H, PhCH_2O), 4.90 (d, *J* = 1.9 Hz, 1H, H-1'''), 4.82 (d, *J* = 10.8 Hz, 1H, PhCH_2O), 4.79 (d, *J* = 10.8 Hz, 1H, PhCH_2O), 4.72 (d, *J* = 10.6 Hz, 1H, PhCH_2O), 4.62 (d, *J* = 12.1 Hz, 1H, PhCH_2O), 4.58 (d, *J* = 11.8 Hz, 1H, PhCH_2O), 4.49 (d, *J* = 11.9 Hz, 1H, PhCH_2O), 4.464 (d, *J* = 11.8 Hz, 1H, PhCH_2O), 4.460 (d, *J* = 11.8 Hz, 1H, PhCH_2O), 4.40 (d, *J* = 12.0 Hz, 1H, PhCH_2O), 4.34 – 4.29 (m, 3H, H-3'', H-4'', PhCH_2O), 4.28 – 4.22 (m, 2H, **-CH_2**-CH=CH_2, PhCH_2O), 4.11 (ddt, *J* = 12.7, 5.7, 1.5 Hz, 1H, **-CH_2**-CH=CH_2), 4.01 – 3.96 (m, 2H, H-3', H-2''), 3.95 (t, *J* = 9.0 Hz, 1H, H-5), 3.88 (dt, *J* = 10.0, 3.0 Hz, 1H, H-5'),

3.82 (dd, *J* = 10.4, 2.0 Hz, 1H, H-5''), 3.80 – 3.75 (m, 3H, H-6', H-3''', H-5'''), 3.69 – 3.64 (m, 2H, H-6', H-6'''), 3.63 – 3.57 (m, 2H, H-4, H-5''), 3.46-3.41 (m, 2H, H-1, H-3), 3.37 – 3.35 (m, 1H, H-2'''), 3.30 (t, *J* = 9.3 Hz, 1H, H-6), 3.25 (dd, *J* = 10.0, 9.0 Hz, 1H, H-4'), 3.13 – 3.10 (m, 1H, H-4'''), 2.90 (dd, *J* = 10.4, 3.7 Hz, 1H, H-2'), 2.86 (dd, *J* = 13.0, 3.7 Hz, 1H, H-6'''), 2.23 (dt, *J* = 13.1, 4.6 Hz, 1H, H-2eq), 1.40 (q, *J* = 13.1 Hz, 1H, H-2ax). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.3, 138.0, 137.9, 137.5, 137.0, 136.9 (Ar), 134.7 (-CH_2-**CH**=CH_2), 128.7, 128.5, 128.42, 128.39, 128.34, 128.27, 128.26, 128.19, 127.83, 127.79, 127.75, 127.70, 127.55, 127.49, 127.1 (Ar), 116.8 (-CH_2-CH=**CH_2**), 106.2 (C-1''), 98.6 (C-1'''), 95.7 (C-1'), 84.2 (C-6), 82.5 (C-2''), 82.1 (C-3''), 82.0 (C-5), 79.5 (C-3'), 77.5 (C-4'), 75.5 (C-4''), 75.3 ($PhCH_2O$), 75.0 ($PhCH_2O$), 74.9 (C-4), 74.4 (C-5'''), 73.6 ($PhCH_2O$), 73.2 ($PhCH_2O$), 73.1 ($PhCH_2O$), 72.8 (C-3'''), 72.4 ($PhCH_2O$), 71.7 ($PhCH_2O$), 71.6 (C-5'), 71.5 ($PhCH_2O$), 70.3 (C-5''), 63.1 (C-2'), 61.5 (C-6'), 60.3 (C-1), 60.1 (C-3), 57.3 (C-2'''), 51.1 (C-6'''), 32.5 (C-2). ESI-HRMS: *m/z* calc for $C_{68}H_{75}N_{15}O_{14}Na$ $[M+Na]^+$ 1348.5516, found 1348.5515.

4-*O*-(2-Azido-3-*O*-benzyl-4,8-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-nona-7-enopyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (20(ax)), and 4-*O*-(2-Azido-3-*O*-benzyl-4,8-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-nona-7-enopyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (20(eq)).

To a stirred solution of DMSO (0.38 mL 5.4 mmol) in 2 mL DCM at -78 °C under argon was added oxalyl chloride (0.22 mL, 2.6 mmol). After stirring for 10 mins, a solution of compound **18** (1.70 g, 1.28 mmol) in DCM (11 mL) and added dropwise. After an additional 3 h Et_3N (0.75 mL, 5.4 mmol) was added. The reaction mixture was stirred for an additional 2 h then diluted with Et_2O, washed with aqueous NH_4Cl solution, DI water, and brine. The organic layer was concentrated under vacuum to give the intermediate aldehyde as a white foam which was used in the next step without further purification. ESI-HRMS: *m/z* calc for $C_{69}H_{77}N_{15}O_{15}Na$ $[M+Na+MeOH]^+$ 1378.5621, found 1378.5647. To a stirred solution of

aldehyde in THF (26 mL) at -78 °C was added vinylMgBr solution (5.2 mL, 1 M in THF). After stirring for 1 h the reaction was quenched with aqueous saturated NH_4Cl solution, diluted with Et_2O, washed with aqueous saturated NH_4Cl solution, brine, dried with Na_2SO_4, and concentrated. The crude residue was purified using silica gel column chromatography (15-25% EtOAc in hexanes) to give an inseparable mixture of diastereomers **19** (0.83 g, 0.614 mmol) in 48% yield. **19**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.17 (m, 60H, Ar-H), 6.13 – 6.10 (m, 2H, H-1'a, H-1'b), 6.03 – 5.84 (m, 4H, CH_2=CH-), 5.70 (d, *J* = 5.7 Hz, 1H, H-1'b), 5.68 (d, *J* = 5.5 Hz, 1H, H-1'a), 5.43 – 5.38 (m, 1H, CH_2=CH-CH_2), 5.36 (dt, *J* = 17.4, 1.6 Hz, 1H, CH_2=CH-CH_2), 5.31 – 5.22 (m, 5H), 5.19 – 5.14 (m, 2H), 5.03 – 4.98 (m, 2H), 4.96 – 4.91 (m, 2H), 4.86 – 4.82 (m, 3H), 4.79 (d, *J* = 10.7 Hz, 1H), 4.77 – 4.72 (m, 2H), 4.67 – 4.63 (m, 2H), 4.62 – 4.57 (m, 2H), 4.54 (d, *J* = 11.7 Hz, 1H), 4.52 – 4.47 (m, 4H), 4.47 – 4.45 (m, 1H), 4.45 – 4.42 (m, 2H), 4.39 – 4.25 (m, 13H), 4.22 – 4.16 (m, 1H), 4.12 (dd, *J* = 10.1, 3.2 Hz, 1H), 4.10 – 4.06 (m, 1H), 4.04 – 3.98 (m, 4H), 3.98 – 3.91 (m, 3H), 3.87 – 3.77 (m, 6H), 3.72 – 3.64 (m, 3H), 3.63 – 3.59 (m, 2H), 3.55 (t, *J* = 9.3 Hz, 1H), 3.50 – 3.42 (m, 4H), 3.39 (m, 2H, H-2'''a, H-2'''b), 3.37 – 3.27 (m, 3H), 3.21 – 3.16 (m, 1H), 3.15 (m, 2H, H-4'''a, H-4'''b), 2.96 (dd, *J* = 10.3, 3.7 Hz, 1H), 2.92 – 2.87 (m, 3H), 2.25 (m, 2H, H-2eqa, H-2eq b), 1.44 (q, *J* = 12.7 Hz, 1H, H-2ax a), 1.36 (q, *J* = 12.7 Hz, 1H, H-2axb). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6, 138.4, 138.1, 138.0, 137.6, 137.02, 136.95, 136.0, 134.7, 134.5, 128.7, 128.54, 128.45, 128.43, 128.38, 128.30, 128.23, 128.19, 128.15, 127.86, 127.84, 127.83, 127.78, 127.71, 127.6, 127.5, 127.2, 127.1 (Ar), 117.0 (CH_2=CH-CH_2), 116.8 (CH_2=CH-CH_2), 116.6 (CH_2=CH-CH_2), 115.4 (CH_2=CH-CH_2), 106.3 (C-1''), 106.2 (C-1''), 98.7 (C-1'''), 98.6 (C-1'''), 95.73 (C-1'), 95.66 (C-1'), 84.3, 84.1, 82.4, 82.3, 82.2, 82.1, 82.08, 81.97, 80.2, 79.8, 78.8, 77.9, 75.6, 75.5, 75.3, 75.2, 75.07, 75.05, 74.9, 74.5, 74.4, 73.8, 73.4, 73.23, 73.16, 73.08, 72.96, 72.90, 72.42, 72.41, 71.7, 71.5, 70.33, 70.27, 70.0, 63.1 (C-2'), 63.0 (C-2'), 60.43 (C-1), 60.39 (C-1), 60.08 (C-3), 60.06 (C-3), 57.3 (C-2'''), 51.2 (C-6'''), 32.6 (C-2), 32.5 (C-2). ESI-HRMS: *m/z* calc for $C_{70}H_{77}N_{15}O_{14}Na$ $[M+Na]^+$ 1374.5672, found 1374.5682. To a stirred solution of compounds **19** (0.83 g 0.614 mmol) in DCM (6.1 mL) was added Hoveyda-Grubbs generation II catalyst (39.2 mg, 0.038 mmol). The reaction

mixture was heated to reflux for 8 h followed by addition of more catalyst (10.7 mg, 0.010 mmol). After an additional 0.5 h the reaction mixture was filtered through silica gel and concentrated. The crude residue was purified using silica gel column chromatography (25-27.5% EtOAc in hexanes) to give **20(ax)** (0.132 g, 0.100 mmol) in 16% isolated yield, **20(eq)** (0.150 g, 0.113 mmol) in 18% isolated yield, and a mixture of diastereomers (0.120 g, 0.091 mmol) in 15% yield. **20(ax)** $[\alpha]_D^{23}$ = 82.9 (*c* = 0.2, DCM), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 21H, ArH), 7.20 – 7.13 (m, 9H, ArH), 6.10 (d, *J* = 3.6 Hz, 1H, H-1'), 5.98 (ddd, *J* = 12.0, 5.7, 2.9 Hz, 1H, H-8'), 5.90 (ddd, *J* = 12.0, 7.2, 2.4 Hz, 1H, H-7'), 5.70 (d, *J* = 6.0 Hz, 1H, H-1''), 5.00 (d, *J* = 10.6 Hz, 1H, $PhCH_2O$), 4.90 (d, *J* = 1.9 Hz, 1H, H-1'''), 4.87 (d, *J* = 11.1 Hz, 1H, $PhCH_2O$), 4.78 (d, *J* = 11.2 Hz, 1H, $PhCH_2O$), 4.69 (d, *J* = 10.6 Hz, 1H, $PhCH_2O$), 4.61 (t, *J* = 11.7 Hz, 2H, $PhCH_2O$), 4.49 (d, *J* = 11.8 Hz, 1H, $PhCH_2O$), 4.47 (s, 2H, $PhCH_2O$), 4.39 (d, *J* = 12.0 Hz, 1H, $PhCH_2O$), 4.35 (dt, *J* = 7.2, 2.4 Hz, 1H, H-6'), 4.34 – 4.28 (m, 3H, 3'', 4'', $PhCH_2O$), 4.23 (d, *J* = 12.1 Hz, 1H, $PhCH_2O$), 4.20 (dd, *J* = 16.1, 5.7 Hz, 1H, H-9'), 4.08 (dt, *J* = 16.1, 2.8 Hz, 1H, H-9'), 4.04 – 3.99 (m, 3H, H-3', H-5', H-2''), 3.96 (t, *J* = 8.9 Hz, 1H, H-5), 3.85 (dd, *J* = 10.4, 2.0 Hz, 1H, H-5''), 3.78 (ddd, *J* = 8.7, 3.7, 1.9 Hz, 1H, H-5'''), 3.75 (t, *J* = 2.9 Hz, 1H, H-3'''), 3.73 (dd, *J* = 9.6, 8.6 Hz, 1H, H-4'), 3.66 (dd, *J* = 13.0, 8.7 Hz, 1H, H-6'''), 3.61 – 3.55 (m, 2H, 4, H-5''), 3.46 – 3.38 (m, 2H, H-1, H-3), 3.36 – 3.33 (m, 1H, H-2'''), 3.29 (t, *J* = 9.3 Hz, 1H, H-6), 3.11 – 3.08 (m, 1H, H-4'''), 2.90 (dd, *J* = 10.5, 3.6 Hz, 1H, H-2'), 2.84 (dd, *J* = 13.0, 3.7 Hz, 1H, H-6'''), 2.22 (dt, *J* = 13.2, 4.6 Hz, 1H, H-2eq), 1.90 (d, *J* = 2.4 Hz, 1H, 6'-OH), 1.38 (q, *J* = 12.8 Hz, 1H, H-2ax). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.5, 138.3, 137.9, 137.5, 137.0, 136.9, 135.4 (C-8'), 128.7, 128.5, 128.4, 128.33, 128.30, 128.29, 128.23, 128.19, 128.0, 127.81, 127.76, 127.69, 127.63, 127.58, 127.46 (Ar), 127.0 (C-7'), 126.9 (Ar), 106.0 (C-1''), 98.7 (C-1'''), 95.7 (C-1'), 84.3 (C-6), 82.6 (C-2''), 82.3 (C-3''), 81.9 (C-3''), 79.4 (C-5), 77.8 (C-4'), 75.6 (C-4''), 75.4 ($PhCH_2O$), 75.0 ($PhCH_2O$), 74.8 (C-4), 74.4 (C-5'''), 73.2 ($PhCH_2O$), 73.1 ($PhCH_2O$), 72.8 (C-3'''), 72.4 (C-5'), 72.3 ($PhCH_2O$), 71.7 ($PhCH_2O$), 71.4 (C-4'''), 70.3 (C-5''), 68.7 (C-6'), 67.5 (C-9'), 62.2 (C-2'), 60.3 (C-1), 60.2 (C-3), 57.2 (2'''), 51.1 (C-6'''), 32.6 (C-2). ESI-HRMS: *m/z* calc for $C_{68}H_{73}N_{15}O_{14}Na$ $[M+Na]^+$ 1346.5359, found 1346.5327. **20(eq)** $[\alpha]_D^{23}$ = 68.0 (*c* = 1.0, $CHCl_3$), ^{1}H NMR (600

MHz, $CHCl_3$) δ 7.39 – 7.23 (m, 21H, ArH), 7.22 – 7.15 (m, 9H, ArH), 6.18 (d, *J* = 3.6 Hz, 1H, H-1'), 5.85 (ddt, *J* = 12.2, 6.0, 3.0 Hz, 1H, H-8'), 5.79 (dt, *J* = 12.2, 2.2 Hz, 1H, H-7'), 5.68 (d, *J* = 5.7 Hz, 1H, H-1''), 4.98 (d, *J* = 10.6 Hz, 1H, $PhCH_2O$), 4.90 (d, *J* = 1.9 Hz, 1H, H-1'''), 4.87 (d, *J* = 11.0 Hz, 1H, $PhCH_2O$), 4.77 (d, *J* = 11.1 Hz, 1H, $PhCH_2O$), 4.73 (d, *J* = 10.6 Hz, 1H, $PhCH_2O$), 4.63 (d, *J* = 12.1 Hz, 1H, $PhCH_2O$), 4.56 (d, *J* = 11.8 Hz, 1H, $PhCH_2O$), 4.49 (d, *J* = 11.8 Hz, 1H, $PhCH_2O$), 4.45 (d, *J* = 11.7 Hz, 2H, $PhCH_2O$), 4.41 (d, *J* = 12.0 Hz, 1H, $PhCH_2O$), 4.32 (dd, *J* = 7.6, 4.3 Hz, 3H, H-3'', H-4''), 4.28 – 4.23 (m, 2H, 9', $PhCH_2O$), 4.19 – 4.15 (m, 1H, H-6'), 4.01 – 3.93 (m, 3H, H-5, H-3', H-2''), 3.86 (dq, *J* = 15.7, 2.6 Hz, 1H, H-9'), 3.83 – 3.78 (m, 2H, H-5'', H-5'''), 3.77 – 3.72 (m, 2H, H-5', H-3'''), 3.67 (dd, *J* = 13.0, 8.7 Hz, 1H, H-6'''), 3.62 – 3.56 (m, 2H, H-4, H-5''), 3.48 – 3.40 (m, 2H, H-1, H-3), 3.38 – 3.36 (m, 1H, H-2'''), 3.30 (t, *J* = 9.3 Hz, 1H, H-6), 3.17 (dd, *J* = 9.6, 8.5 Hz, 1H, H-4'), 3.12 (t, *J* = 2.7 Hz, 1H, H-4'''), 3.00 (dd, *J* = 10.4, 3.6 Hz, 1H, H-2'), 2.86 (dd, *J* = 13.0, 3.7 Hz, 2H, H-6'''), 2.22 (dt, *J* = 13.2, 4.6 Hz, 1H, H-2eq), 1.42 (q, *J* = 12.7 Hz, 1H, H-2ax) ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.4, 138.3, 137.9, 137.5, 137.0, 136.9, 132.7 (C-7'), 128.7 (Ar), 128.6 (C-8'), 128.5, 128.4, 128.35, 128.32, 128.27, 128.21, 128.1, 127.84, 127.82, 127.77, 127.74, 127.6, 127.51, 127.50, 127.2 (Ar), 106.1 (C-1''), 98.6 (C-1'''), 94.8 (C-1'), 84.2 (C-6), 83.8 (C-4'), 82.4 (C-2''), 82.1 (C-3''), 82.0 (C-5), 77.8 (C-3'), 75.6 ($PhCH_2O$), 75.4 (C-4''), 75.0 (C-4), 74.5 (C-5'''), 73.7 (C-6'), 73.2 ($PhCH_2O$), 73.1 ($PhCH_2O$), 72.8 (C-3'''), 72.4 ($PhCH_2O$), 72.0 (C-5'), 71.7 ($PhCH_2O$), 71.5 (C-4'''), 70.3 (C-5''), 67.7 (C-9'), 62.5 (C-2'), 60.3 (C-3), 60.2 (C-2), 57.2 (C-2'''), 51.1 (C-6'''), 32.4 (C-2). ESI-HRMS: *m/z* calc for $C_{68}H_{73}N_{15}O_{14}Na$ $[M+Na]^+$ 1346.5359, found 1346.5348.

4-*O*-(2-Amino-4,9-anhydro-2,7,8-trideoxy-D-glycero-α-D-gluco-nonapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (9).

To a solution of compound **20(ax)** (30.0 mg, 0.023 mmol) in 1:1 1,4-dioxane/10% aqueous AcOH (0.6 mL) was added Pd/C (10 wt%, 64.8 mg). The reaction mixture was stirred under 50 psi H_2 for 26 h before filtration through Celite and concentration. The crude residue was purified using CM Sephadex ion exchange column chromatography (0.1-0.7% aqueous NH_4OH) followed by lyophilization with acetic acid

to give the pentaacetate salt **9** (6.8 mg, 0.0071 mmol) in 31% yield as a white powder. $[\alpha]_D^{23}$ = 13.3 (*c* = 0.03, water), ^{1}H NMR (600 MHz, D_2O) δ 5.64 (d, *J* = 3.9 Hz, 1H, H-1'), 5.22 (d, *J* = 2.3 Hz, 1H, H-1''), 5.12 (d, *J* = 1.8 Hz, 1H, H-1'''), 4.36 (dd, *J* = 6.9, 4.9 Hz, 1H, H-3''), 4.23 (dd, *J* = 4.9, 2.3 Hz, 1H, H-2''), 4.14 (ddd, *J* = 6.9, 4.0, 1.5 Hz, 1H, H-5'''), 4.05-4.08 (m, 3H, H-6', H-4'', H-3'''), 3.77 – 3.73 (m, 2H, H-3', H-5''), 3.72 – 3.67 (m, 2H, H-5, H-9'), 3.67 – 3.59 (m, 3H, H-4, H-5'', H-4'''), 3.50 (dd, *J* = 10.0, 3.4 Hz, 1H, H-5'), 3.47 (dd, *J* = 10.5, 9.1 Hz, 1H, H-6), 3.41 (dt, *J* = 3.0, 1.3 Hz, 1H, H-2'''), 3.36 (t, *J* = 9.4 Hz, 1H, H-4'), 3.26 (dd, *J* = 13.7, 6.7 Hz, 1H, H-6'''), 3.20 (dd, *J* = 13.7, 3.9 Hz, 1H, H-6'''), 3.16 (dd, *J* = 11.0, 3.9 Hz, 1H, H-2'), 3.11 (m, 2H, H-1, H-3), 2.17 (dt, *J* = 12.7, 4.3 Hz, 1H, H-2eq), 1.93 (m, 1H, H-8'), 1.84 – 1.77 (m, 1H, H-7'), 1.75 (s, 15H, AcOH), 1.58 – 1.46 (m, 3H, H-2ax, H-7', H-8'). ^{13}C NMR (151 MHz, D_2O) δ 179.7 (AcOH), 108.6 (C-1''), 94.3 (C-1'), 94.0 (C-1'''), 83.6 (C-5), 79.7 (C-4''), 77.0 (C-4), 73.6 (C-3''), 73.4 (C-5'), 72.9 (C-4'), 72.0 (C-2''), 71.5 (C-6), 68.8 (C-5'''), 67.7 (C-9'), 66.5 (C-6'), 66.4 (C-3'), 66.3 (C-3'''), 65.9 (C-4'''), 58.5 (C-5''), 52.3 (C-2'), 49.4 (C-2'''), 48.7 (C-1), 47.4 (C-3), 39.0 (C-6'''), 28.6 (C-2), 24.5 (C-7'), 21.7 (AcOH), 17.7 (C-8'). ESI-HRMS: *m/z* calc for $C_{26}H_{50}N_5O_{14}$ $[M+H]^+$ 656.3354, found 656.3372.

4-*O*-(2-Amino-4,9-anhydro-2,7,8-trideoxy-L-glycero-α-D-gluco-nonapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (8).

To a solution of compound **20(eq)** (22.8 mg, 0.017 mmol) in 1:1 1,4-dioxane/10% aqueous AcOH (0.6 mL) was added Pd/C (10 wt%, 48.2 mg). The reaction mixture was stirred under 50 psi H_2 for 23 h before filtration through Celite and concentration. The crude residue was purified using CM Sephadex ion exchange column chromatography (0.1-0.8% aqueous NH_4OH) followed by lyophilization with acetic acid to give the pentaacetate salt **8** (2.9 mg, 0.0030 mmol) in 18% yield as a white powder. $[\alpha]_D^{23}$ = 80.4 (*c* = 0.05, water), ^{1}H NMR (600 MHz, D_2O) δ 5.40 (d, *J* = 3.8 Hz, 1H, H-1'), 5.22 (d, *J* = 3.2 Hz, 1H, H-1''), 5.14 (d, *J* = 1.9 Hz, 1H, H-1'''), 4.36 (t, *J* = 5.7 Hz, 1H, H-3''), 4.19 – 4.15 (m, 2H, H-2'', H-5'''), 4.08 (t, *J* = 3.2 Hz, 1H, H-3'''), 4.07 – 4.04 (m, 1H, H-4''), 3.75 (dd, *J* = 12.4, 3.2 Hz, 1H, H-5''), 3.74 – 3.58 (m, 6H, H-4, H-5, H-3', H-9', H-5'', H-4'''), 3.53 – 3.39 (m, 4H, H-6, H-5', H-6', H2'''), 3.29 (dd, *J* = 13.6, 6.8 Hz, 1H, H-6'''), 3.25

– 3.18 (m, 2H, H-4', H-6'''), 3.15 (dd, *J* = 10.8, 3.8 Hz, 1H, H-2'), 3.13 – 3.07 (m, 2H, H-1, H-3), 2.16 (dt, *J* = 12.9, 4.3 Hz, 1H, H-2eq), 1.81 – 1.61 (m, 18H, H-7', H-8', AcOH), 1.57 – 1.44 (m, 2H, H-2ax, H-7'). ^{13}C NMR (151 MHz, D_2O) δ 181.3 (AcOH), 109.5 (C-1''), 96.8 (C-1'), 95.8 (C-1'''), 84.1 (C-5), 81.32 (C-4''), 81.28 (C-4), 76.6 (C-5'), 75.3 (C-3''), 74.8 (C-6'), 74.6 (C-4'), 73.3 (C-2''), 73.1 (C-6), 70.2 (C-5'''), 68.9 (C-3'), 68.5 (C-9'), 67.8 (C-3'''), 67.3 (C-4'''), 60.1 (C-5''), 54.1 (C-2'), 50.9 (C-2'''), 50.0 (C-1), 49.3 (C-3), 40.4 (C-6'''), 30.6 (C-2), 28.1 (C-7'), 23.1 (AcOH), 21.9 (C-8'). ESI-HRMS: *m/z* calc for $C_{26}H_{50}N_5O_{14}$ $[M+H]^+$ 656.3354, found 656.3359.

4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,8-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (22(ax)), and 4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,8-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (22(eq)).

1 M BH_3•THF (0.5 mL, 0.5 mmol) was added to a stirred solution of compounds **13** (0.69 g, 0.45 mmol) in THF (4.5 mL) at 0 °C. After 4 h more BH_3•THF (0.1 mL, 0.1 mmol) was added. After a further 2 h, aqueous saturated $NaHCO_3$ solution (1.2 mL) and 30% hydrogen peroxide solution (0.46 mL) were added dropwise. After 1 h the reaction mixture was diluted with Et_2O, washed with $NaHCO_3$ solution and brine, dried with Na_2SO_4, and concentrated. The crude residue was purified using silica gel column chromatography in 25 to 35% EtOAc in hexanes to give compounds **21** (0.292 g, 0.190 mmol) in 42% yield as an inseparable mixture of diastereomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.09 (m, 74H, Ar-H), 6.84 – 6.80 (m, 4H, Ar-H), 6.19 (d, *J* = 3.7 Hz, 1H, H-1'a), 6.16 (d, *J* = 3.7 Hz, 1H, H-1'b), 5.65 (d, *J* = 6.6 Hz, 1H, H-1''a), 5.63 (d, *J* = 6.3 Hz, 1H, H-1''b), 4.98 – 4.94 (m, 2H), 4.89 – 4.72 (m, 10H), 4.67 (d, *J* = 10.7 Hz, 1H), 4.64 – 4.56 (m, 6H), 4.54 (d, *J* = 11.9 Hz, 1H), 4.51 (d, *J* = 11.8 Hz, 1H), 4.49 (d, *J* = 1.8 Hz, 1H), 4.47 (d, *J* = 1.6 Hz, 1H), 4.47 – 4.37 (m, 8H), 4.33 – 4.21 (m, 11H), 4.19 (dd, *J* = 5.0, 2.5 Hz, 1H), 4.11 (td, *J* = 10.6, 8.7 Hz, 2H), 4.06 – 4.03 (m, 1H), 4.02 – 4.00 (m, 1H), 3.97 – 3.88 (m, 4H), 3.87 – 3.81 (m, 2H), 3.80

(s, 3H), 3.77 (s, 3H), 3.73 (dt, *J* = 9.1, 2.8 Hz, 3H), 3.70 – 3.63 (m, 4H), 3.59 – 3.51 (m, 5H), 3.51 – 3.40 (m, 3H), 3.38 – 3.32 (m, 2H), 3.32 – 3.30 (m, 1H), 3.28 (d, *J* = 9.3 Hz, 1H), 3.17 (t, *J* = 9.5 Hz, 1H), 3.13 – 3.07 (m, 4H), 2.92 – 2.87 (m, 2H), 2.82 (dd, *J* = 13.0, 3.7 Hz, 1H), 2.23 (dt, *J* = 13.1, 4.6 Hz, 1H, H-2eq a), 2.09 (dt, *J* = 13.5, 4.8 Hz, 1H, H-2eq b), 2.07 – 2.00 (m, 2H, H-7'a, H-7'b), 1.87 (m, 2H, H-7'a, H-7'b), 1.36 (q, *J* = 12.7 Hz, 1H, H-2ax a), 1.00 (q, *J* = 12.8 Hz, 1H, H-2ax b). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 159.0, 138.3, 138.2, 138.14, 138.12, 138.0, 137.92, 137.87, 137.6, 137.5, 137.03, 137.00, 136.96, 136.94, 129.8, 128.8, 128.66, 128.65, 128.50, 128.47, 128.41, 128.39, 128.36, 128.34, 128.31, 128.22, 128.17, 128.16, 128.11, 127.90, 127.85, 127.81, 127.77, 127.74, 127.5, 127.2, 113.8, 113.7 (Ar), 106.0 (C-1'a), 105.9 (C-1'b), 98.7 (C-1'''a, C-1'''b), 95.8 (C-1'b), 95.4 (C-1'a), 84.14, 84.10, 82.6, 82.3, 82.10, 81.97, 81.70, 80.8, 80.5, 77.9, 77.5, 75.9, 75.62, 75.56, 75.4, 75.3, 75.03, 75.00, 74.9, 74.5, 74.4, 74.2, 74.0, 73.90, 73.85, 73.4, 73.3, 73.2, 72.9, 72.8, 72.6, 72.4, 72.3, 71.8, 71.73, 71.66, 71.4, 70.9, 70.34, 70.29, 69.9, 63.2, 63.1, 60.7, 60.42, 60.37, 60.29, 59.58, 57.3, 57.2, 55.3, 55.2, 51.1, 50.9, 33.0, 32.7, 32.5, 30.9, 21.0, 14.2. ESI-HRMS: m/z calcd for $C_{82}H_{89}N_{15}O_{16}Na$ $[M + Na]^+$ 1562.6509, found 1562.6514. TsCl (58.3 mg, 0.306 mmol) was added to a stirred solution of compounds **21** (0.292 g, 0.190 mmol) and Hunig's base (0.07 mL, 0.4 mmol) in DCM (1.9 mL). Further Hunig's base (0.19 mL, 0.71 mmol) and TsCl (0.227 g, 1.19 mmol) were added after 24 h and the reaction mixture stirred for a total of 4 days before it was diluted with Et_2O and washed with 1N HCl, $NaHCO_3$ solution, and brine. The organic layer was dried with Na_2SO_4, filtered, and concentrated. The crude residue was passed through silica gel and used in the next step without further purification. ESI-HRMS: m/z calcd for $C_{89}H_{95}N_{15}O_{18}SNa$ $[M + Na]^+$ 1717.6628, found 1717.6620. To a stirred solution of the 8'-OTs compounds in DCM (1.68 mL) at 0 ^{o}C was added TFA (0.19 mL). After 50 mins the reaction mixture was diluted with Et_2O and washed with water, saturated $NaHCO_3$ solution, and brine. The organic layer was dried with Na_2SO_4, filtered, and concentrated to give a mixture of diastereomers which were passed through silica gel and used in the next step without further purification. ESI-HRMS: m/z calcd for $C_{81}H_{87}N_{15}O_{17}SNa$ $[M + Na]^+$ 1596.6023, found 1596.6086. The crude

residue was stirred in DMF at 0 °C followed by addition of 60% NaH in mineral oil (8.0 mg, 0.2 mmol). After 1.5 h the reaction was quenched with NH_4Cl solution (1 mL), diluted with Et_2O, and washed with DI water and brine. The organic layer was dried with Na_2SO_4 and concentrated. The crude residue was purified using silica gel column chromatography in 12.5% EtOAc in hexanes to give **22(ax)** (22.6 mg, 0.0161 mmol) in 9% yield as the less polar diastereomer and **22(eq)** (26.4 mg, 0.0188 mmol) in 10% yield as the more polar diastereomer. **22(ax)** $[\alpha]_D^{23}$ = 71.5 (*c* = 1.0, DCM), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.10 (m, 35H, Ar-H), 6.03 (d, *J* = 3.8 Hz, 1H, H-1'), 5.63 (d, *J* = 5.2 Hz, 1H, H-1''), 4.95 (d, *J* = 9.5 Hz, 1H, $PhCH_2O$), 4.93 (d, *J* = 10.2 Hz, 1H, $PhCH_2O$), 4.82 (d, *J* = 1.9 Hz, 1H, H-1'''), 4.76 – 4.72 (m, 2H, $PhCH_2O$), 4.71 (d, *J* = 10.8 Hz, 1H, $PhCH_2O$), 4.63 (d, *J* = 12.2 Hz, 1H, $PhCH_2O$), 4.60 (d, *J* = 12.1 Hz, 1H, $PhCH_2O$), 4.54 (d, *J* = 10.9 Hz, 1H, $PhCH_2O$), 4.52 (d, *J* = 10.4 Hz, 1H, $PhCH_2O$), 4.44 – 4.38 (m, 3H, $PhCH_2O$), 4.31 (d, *J* = 12.0 Hz, 1H, $PhCH_2O$), 4.29 – 4.23 (m, 3H, H-3'', H-4'', $PhCH_2O$), 4.02 – 3.88 (m, 5H, H-5, H-3', H-5', H-6', H-2''), 3.85 – 3.80 (m, 2H, H-4', H-8'), 3.78 – 3.71 (m, 4H, H-8', H-5'', H-3''', H-5'''), 3.65 (dd, *J* = 9.8, 8.6 Hz, 1H, H-4), 3.60 – 3.53 (m, 2H, H-5'', H-6'''), 3.45 – 3.38 (m, 2H, H-1, H-3), 3.33 (t, *J* = 2.7 Hz, 1H, H-2'''), 3.28 (t, *J* = 9.2 Hz, 1H, H-6), 3.14 (dd, *J* = 10.2, 3.8 Hz, 1H, H-2'), 3.12 (t, *J* = 2.8 Hz, 1H, H-4'''), 2.92 (dd, *J* = 12.9, 4.3 Hz, 1H, H-6'''), 2.23 (dt, *J* = 13.1, 4.6 Hz, 1H, H-2eq), 1.93 – 1.88 (m, 1H, H-7'eq), 1.78 (tdd, *J* = 13.9, 5.5, 2.2 Hz, 1H, H-7'ax), 1.41 (q, *J* = 12.7 Hz, 1H, H-2ax). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.1, 138.5, 138.2, 137.8, 137.6, 137.03, 136.95, 128.7, 128.5, 128.4, 128.33, 128.30, 128.29, 128.25, 128.15, 128.0, 127.8, 127.7, 127.54, 127.48, 127.46, 127.41, 127.3, 127.1 (Ar), 106.2 (C-1''), 98.6 (C-1'''), 96.8 (C-1'), 83.8 (C-6), 82.1 (C-2''), 82.0 (C-4''), 81.5 (C-5), 77.7 (C-3'), 76.3 (C-4'), 75.5 (C-3''), 75.4 (C-4), 75.0 ($PhCH_2O$), 74.8 ($PhCH_2O$), 74.2 (C-5'''), 73.2 ($PhCH_2O$), 73.02 ($PhCH_2O$), 72.97 (C-3'''), 72.4 ($PhCH_2O$), 72.3 (C-6'), 71.9 ($PhCH_2O$), 71.8 ($PhCH_2O$), 71.5 (C-4'''), 70.6 (C-5'), 70.0 (C-5''), 62.6 (C-2'), 62.3 (C-8'), 60.3 (C-1), 59.9 (C-3), 57.4 (C-2'''), 51.0 (C-6'''), 32.4 (C-2), 31.1 (C-7'). ESI-HRMS: m/z calcd for $C_{74}H_{83}N_{16}O_{14}$ $[M + NH_4]^+$ 1419.6275, found 1419.6295. **22(eq)** $[\alpha]_D^{23}$ = 79.5 (*c* = 1.0, DCM), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.05 (m, 35H, Ar-H), 6.25 (d, *J* = 3.8 Hz, 1H, H-1'), 5.68 (d, *J* = 6.2 Hz, 1H, H-1''), 4.94 – 4.88 (m, 4H, H-

1’’’, $PhCH_2O$), 4.77 (d, *J* = 11.8 Hz, 1H, $PhCH_2O$), 4.71 (d, *J* = 11.1 Hz, 1H, $PhCH_2O$), 4.63 – 4.59 (m, 2H, $PhCH_2O$), 4.58 (d, *J* = 11.8 Hz, 1H, $PhCH_2O$), 4.52 (d, *J* = 11.7 Hz, 1H, $PhCH_2O$), 4.46 – 4.41 (m, 2H, $PhCH_2O$) 4.40 (d, *J* = 12.0 Hz, 1H, $PhCH_2O$), 4.30 (d, *J* = 12.0 Hz, 1H, $PhCH_2O$), 4.28 – 4.25 (m, 2H, H-3’’, H-4’’), 4.23 (d, *J* = 12.1 Hz, 1H, $PhCH_2O$), 4.04 – 3.90 (m, 4H, H-5, H-3’, H-8’, H-2’’), 3.82 (t, *J* = 9.3 Hz, 1H, H-5’), 3.79 (dd, *J* = 10.4, 2.1 Hz, 1H, H-5’’), 3.77 – 3.73 (m, 2H, H-3’’’, H-5’’’), 3.72 (t, *J* = 9.4 Hz, 1H, H-4), 3.64 (dd, *J* = 13.0, 8.6 Hz, 1H, H-6’’’), 3.56 (dd, *J* = 10.4, 2.8 Hz, 1H, H-5’’), 3.51 (ddd, *J* = 11.1, 8.8, 5.2 Hz, 1H, H-6’), 3.44 (ddd, *J* = 12.6, 9.8, 4.5 Hz, 1H, H-3), 3.40 – 3.32 (m, 3H, H-1, H-8’, H-2’’’), 3.09 (t, *J* = 2.4 Hz, 1H, H-4’’’), 3.03 – 2.99 (m, 2H, H-6, H-2’), 2.95 (t, *J* = 9.4 Hz, 1H, H-4’), 2.82 (dd, *J* = 13.0, 3.7 Hz, 1H, H-6’’’), 2.14 (dt, *J* = 13.2, 4.6 Hz, 1H, H-2eq), 2.07 – 2.03 (m, 1H, H-7’eq), 1.78 (tdd, *J* = 13.0, 11.1, 5.1 Hz, 1H, H-7’ax), 1.22 (q, *J* = 12.7 Hz, 1H, H-2ax). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.3, 138.4, 138.3, 138.0, 137.4, 137.0, 136.9, 128.7, 128.5, 128.43, 128.41, 128.32, 128.27, 128.22, 128.17, 128.0, 127.81, 127.77, 127.70, 127.6, 127.5, 127.4, 127.2, 127.1 (Ar), 105.8 (C-1’’), 98.6 (C-1’’’), 95.3 (C-1’), 84.3 (C-6), 82.8 (C-2’’), 82.1 (C-4’’), 81.6 (C-5), 80.8 (C-4’), 77.3 (C-3’), 76.8 (C-6’), 75.5 (C-3’’), 75.00 ($PhCH_2O$), 74.96 ($PhCH_2O$), 74.4 (C-5’’’), 74.1 (C-4), 73.4 ($PhCH_2O$), 73.2 ($PhCH_2O$), 73.0 (C-5’), 72.8 (C-3’’’), 72.3 ($PhCH_2O$), 72.1 ($PhCH_2O$), 71.7 ($PhCH_2O$), 71.4 (C-4’’’), 70.3 (C-5’’), 66.1 (C-8’), 62.9 (C-2’), 60.3 (C-1), 60.0 (C-3), 57.2 (C-2’’’), 51.1 (C-6’’’), 32.5 (C-2), 32.1 (C-7’). ESI-HRMS: m/z calcd for $C_{74}H_{79}N_{15}O_{14}$ $[M + Na]^+$ 1424.5829, found 1424.5869.

4-*O*-(2-Amino-4,8-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (11)).

To a solution of compound **22(ax)** (21.1 mg, 0.015 mmol) in 1:1 1,4-dioxane/10% aqueous AcOH (0.6 mL) was added Pd/C (10 wt%, 43.4 mg). The reaction mixture was stirred under 50 psi H_2 for 19 h before filtration through Celite and concentration. The crude residue was purified using CM Sephadex ion exchange column chromatography (0.1-0.8% aqueous NH_4OH) followed by lyophilization with excess acetic acid to give the pentaacetate salt **11** (6.0 mg, 0.0064 mmol) in 43% yield as a white powder. $[\alpha]_D^{23}$

= 22.1 (*c* = 0.1, water), ^{1}H NMR (600 MHz, D_2O) δ 5.62 (d, *J* = 4.1 Hz, 1H, H-1'), 5.23 (d, *J* = 2.2 Hz, 1H, H-1''), 5.13 (d, *J* = 1.8 Hz, 1H, H-1'''), 4.38 (dd, *J* = 7.0, 4.9 Hz, 1H, H-3''), 4.24 (dd, *J* = 4.8, 2.1 Hz, 1H, H-2''), 4.17 – 4.14 (m, 1H, H-5'''), 4.10 – 4.03 (m, 3H, H-6', H-4'', H-3'''), 3.81 (t, *J* = 10.1 Hz, 1H, H-3'), 3.77 (dd, *J* = 12.4, 2.9 Hz, 1H, H-5''), 3.72 – 3.65 (m, 3H, H-5, H-8', H-4'''), 3.65 – 3.58 (m, 3H, H-5', H-8', H-5''), 3.56 (t, *J* = 9.4 Hz, 1H, H-4), 3.48 – 3.38 (m, 3H, H-6, H-4', H-2'''), 3.27 (dd, *J* = 13.6, 6.8 Hz, 1H, H-6'''), 3.24 – 3.17 (m, 2H, H-2', H-6'''), 3.13 – 3.06 (m, 1H, H-1), 3.06 – 2.99 (m, 1H, H-3), 2.13 (dt, *J* = 12.8, 4.1 Hz, 1H, H-2eq), 1.76 (s, 16H, H-7'ax, AcOH), 1.71 – 1.66 (m, 1H, H-7'eq), 1.45 (q, *J* = 12.5 Hz, 1H, H-2ax). ^{13}C NMR (151 MHz, D_2O) δ 181.2 (AcOH), 109.9 (C-1''), 96.5 (C-1'), 95.4 (C-1'''), 85.0 (C-5), 81.0 (C-4''), 79.4 (C-4), 74.9 (C-3''), 73.8 (C-4'), 73.4 (C-2''), 73.1 (C-6), 70.2 (C-5', C-5'''), 67.7 (C-3'''), 67.6 (C-3'), 67.3 (C-4'''), 63.8 (C-6'), 62.3 (C-8'), 59.9 (C-5''), 54.5 (C-2'), 50.9 (C-2'''), 50.2 (C-1), 48.8 (C-3), 40.3 (C-6'''), 31.6 (C-7'), 30.7 (C-2), 23.1 (AcOH). ESI-HRMS: m/z calcd for $C_{25}H_{47}N_5O_{14}$ $[M + H]^+$ 642.3198, found 642.3193.

4-*O*-(2-Amino-4,8-anhydro-2,7-dideoxy-L-glycerol-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (10).

To a solution of compound **22(eq)** (26.4 mg, 0.019 mmol) in 1:1 1,4-dioxane/10% aqueous AcOH (0.6 mL) was added Pd/C (10 wt%, 43.4 mg). The reaction mixture was stirred under 50 psi H_2 for 19 h before filtration through Celite and concentration. The crude residue was purified using CM Sephadex ion exchange column chromatography (0.1-0.8% aqueous NH_4OH) followed by lyophilization with excess acetic acid to give the pentaacetate salt **10** (9.1 mg, 0.0097 mmol) in 51% yield as a white powder. ^{1}H NMR (600 MHz, D_2O) δ 5.53 (d, *J* = 4.1 Hz, 1H, H-1'), 5.22 (d, *J* = 2.7 Hz, 1H, H-1''), 5.13 (d, *J* = 1.8 Hz, 1H, H-1'''), 4.36 (dd, *J* = 6.6, 5.1 Hz, 1H, H-3''), 4.20 (dd, *J* = 5.0, 2.7 Hz, 1H, H-2''), 4.15 (ddd, *J* = 6.6, 4.1, 1.5 Hz, 1H, H-5'''), 4.07 (t, *J* = 3.1 Hz, 1H, H-3'''), 4.05 – 4.02 (m, 1H, H-4''), 3.89 – 3.85 (m, 1H, H-8'), 3.82 (t, *J* = 10.0 Hz, 1H, H-3'), 3.77 – 3.69 (m, 4H, H-4, H-5, H-6', H-5''), 3.66 (dt, *J* = 3.0, 1.4 Hz, 1H, H-4'''), 3.61 (dd, *J* = 12.4, 4.6 Hz, 1H, H-5''), 3.50 (dd, *J* = 10.4, 8.7 Hz, 1H, H-6), 3.44 – 3.37 (m, 3H, H-5', H-8', H-2'''), 3.29 – 3.17 (m, 4H, H-3, H-2', H-6''', H-6'''), 3.14 (td, *J* = 11.5, 10.7, 4.0 Hz, 1H, H-1), 3.06 (t, *J* = 9.5 Hz,

1H, H-4'), 2.24 (dt, *J* = 13.0, 4.3 Hz, 1H, H-2eq), 1.93 – 1.87 (m, 1H, H-7'eq), 1.75 (s, 15H, AcOH), 1.62 – 1.50 (m, 2H, H-2ax, H-7'ax). ^{13}C NMR (151 MHz, D_2O) δ 181.0 (AcOH), 109.7 (C-1''), 96.7 (C-1'), 95.4 (C-1'''), 84.2 (C-5), 81.3 (C-4''), 79.6 (C-4), 78.1 (C-4'), 75.1 (C-3''), 73.6 (C-5'), 73.3 (C-2''), 72.7 (C-6), 70.2 (C-5'''), 68.5 (C-6'), 67.6 (C-3'''), 67.4 (C-3'), 67.2 (C-4'''), 66.0 (C-8'), 59.9 (C-5''), 54.4 (C-2'), 50.8 (C-2'''), 49.8 (C-1), 49.0 (C-3), 40.3 (C-6'''), 33.1 (C-7'), 29.4 (C-2), 23.1 (AcOH). ESI-HRMS: m/z calcd for $C_{25}H_{47}N_5O_{14}$ $[M + H]^+$ 642.3198, found 642.3199.

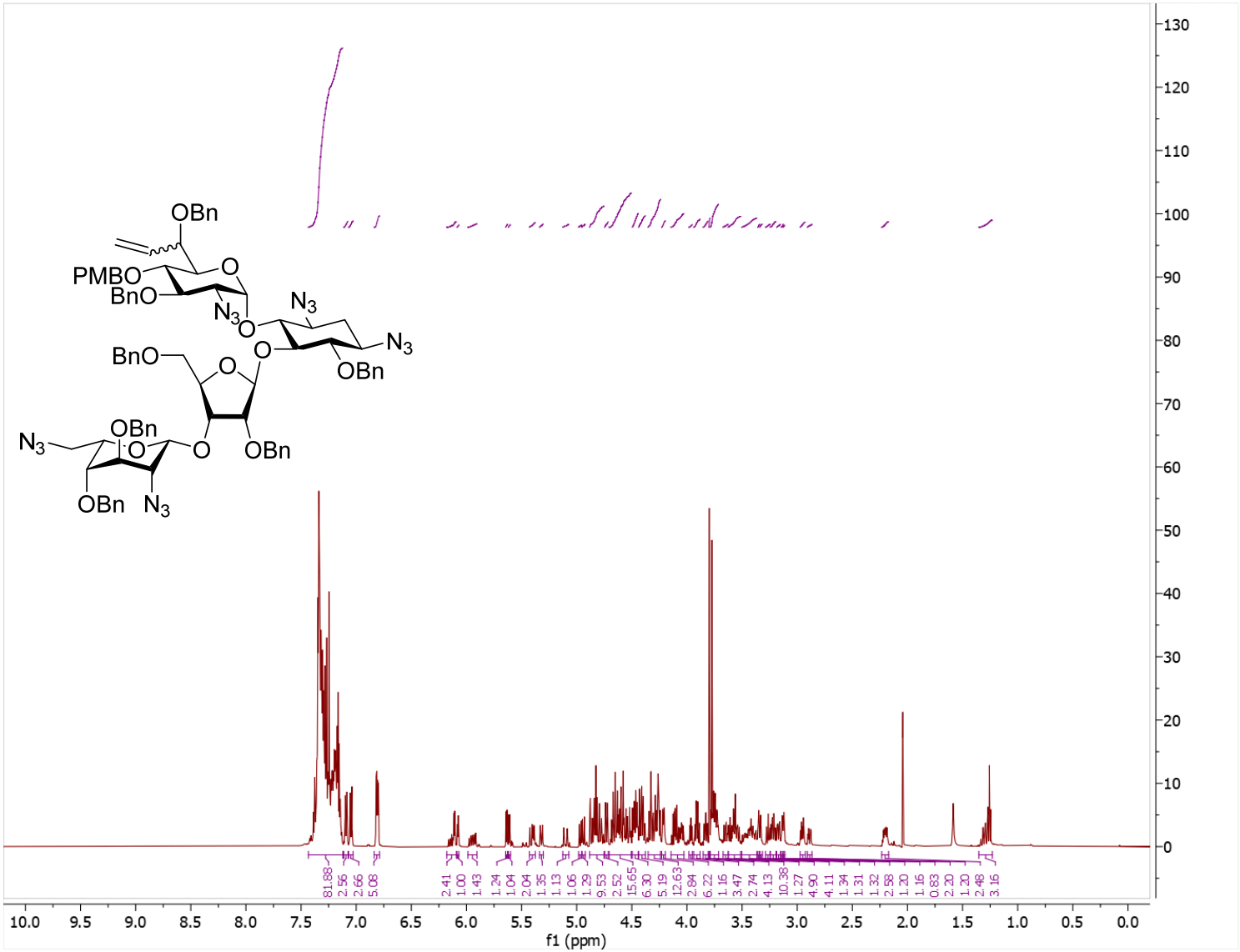
Cell-free translation inhibition assays. The S30 fraction of *Mycobacterium smegmatis* cell extracts was used for bacterial cell-free translation inhibition assays as described previously.[1] Inhibition of mammalian ribosomes has been assessed with a commercial Rabbit Reticulocyte Lysate System (Promega) as described previously.[1] Firefly luciferase mRNA was used as reporter to monitor translation activity. Luminescence was measured using a luminometer Flx800 (Bio-Tek Instruments).

Antibacterial inhibition assays. The minimal inhibitory concentrations (MIC) of synthesized compounds were determined by broth microdilution assays according to CLSI reference methodology M07.[2]

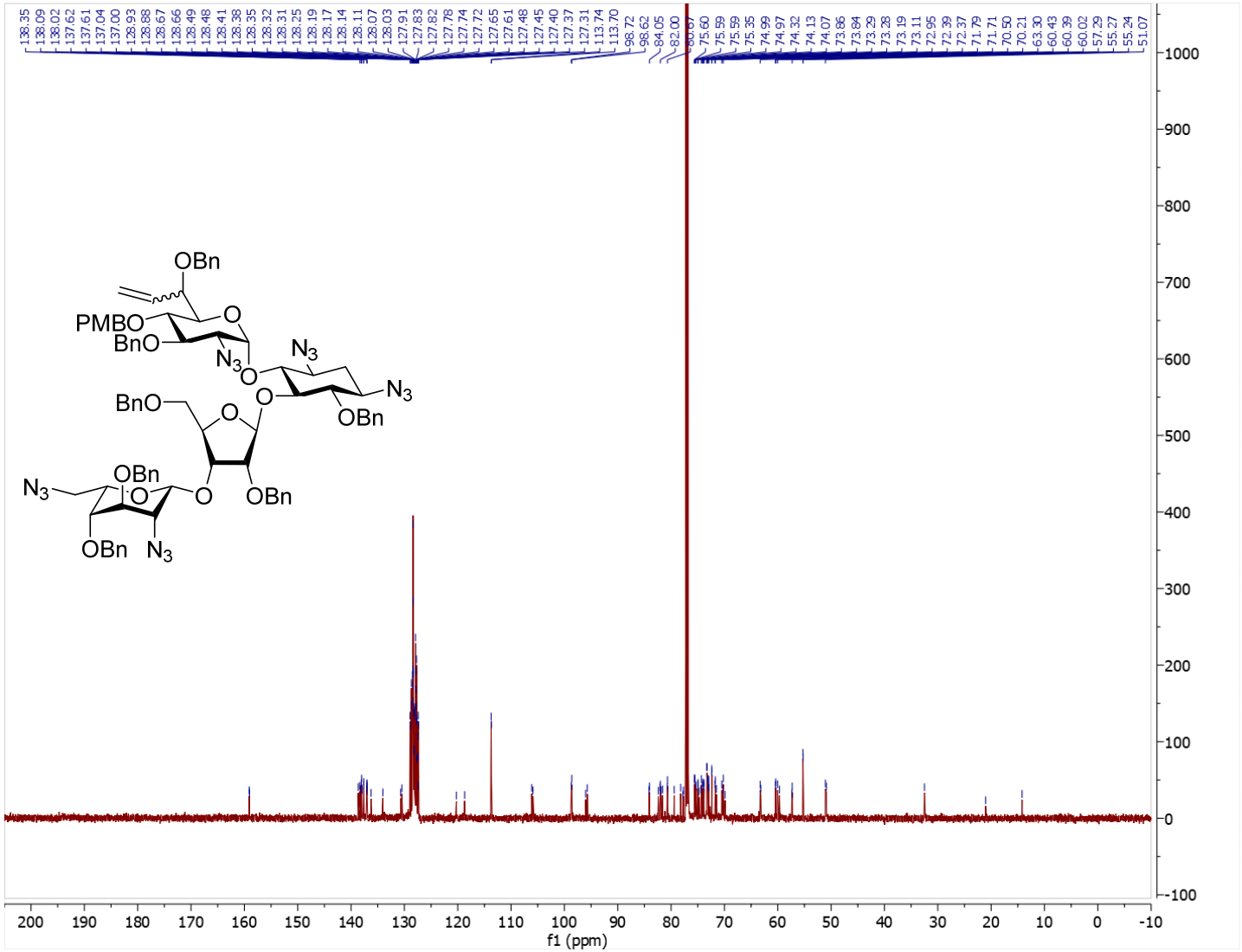
1. Matt, T.; Ng, C. L.; Lang, K.; Sha, S.-H.; Akbergenov, R.; Shcherbakov, D.; Meyer, M.; Duscha, S.; Xie, J.; Dubbaka, S. R.; Perez-Fernandez, D.; Vasella, A.; Ramakrishnan, V.; Schacht, J.; Böttger, E. C. Dissociation of Antibacterial Activity and Aminoglycoside Ototoxicity in the 4-Monosubstituted 2-Deoxystreptamine Apramycin. *Proc. Natl. Acad. Sci., USA* **2012**, *109*, 10984-1098

2. Clinical Laboratory Standards Institute (2015). Methods for Dilution Antimicrobial Susceptibility Tests for Bacteria That Grow Aerobically-Tenth Edition: Approved Standard M07-A10. CLSI, Wayne, PA, USA

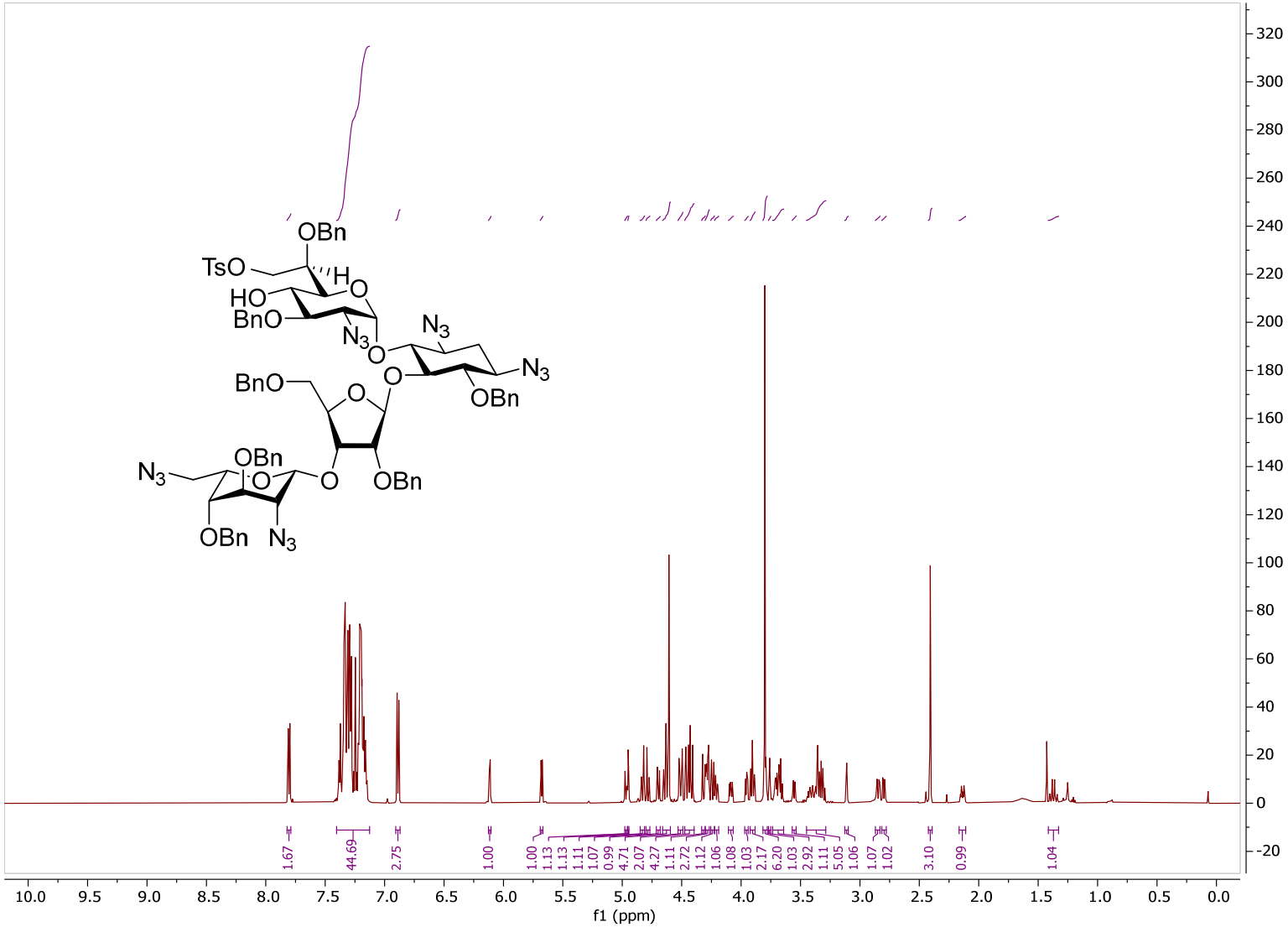
1,3,2',2''',6'''-Pentaazido-6,3',6',2'',5'',3''',4'''-hepta-*O*-benzyl-6'-*C*-vinyl-1,3,2',2''',6'''-pentadeaminoparomomycin (13) ^{1}H NMR (600 MHz, $CDCl_3$)



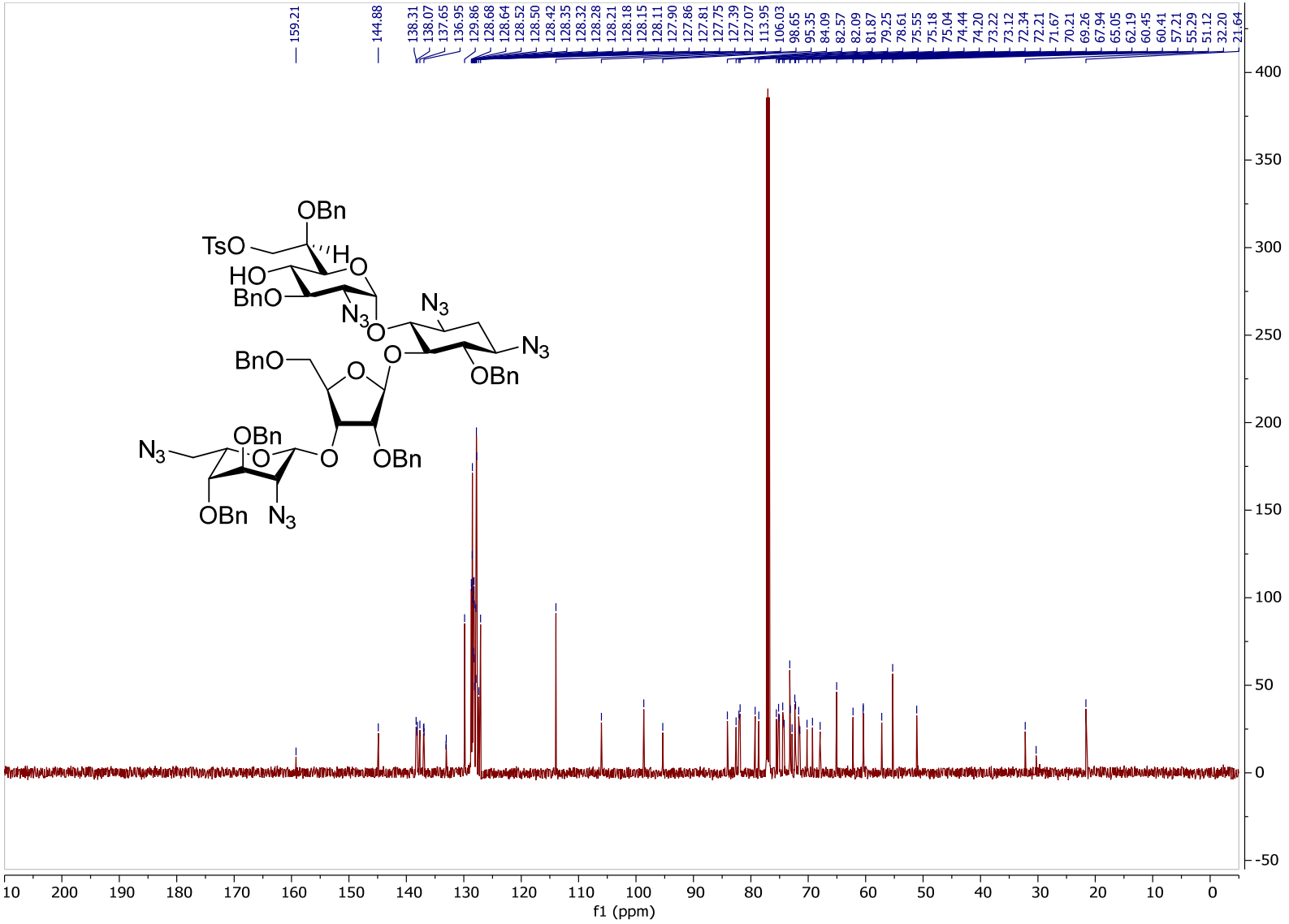
1,3,2',2''',6'''-Pentaazido-6,3',6',2'',5'',3''',4'''-hepta-*O*-benzyl-6'-*C*-vinyl-1,3,2',2''',6'''-pentadeaminoparomomycin (13) ^{13}C NMR (151 MHz, $CDCl_3$)



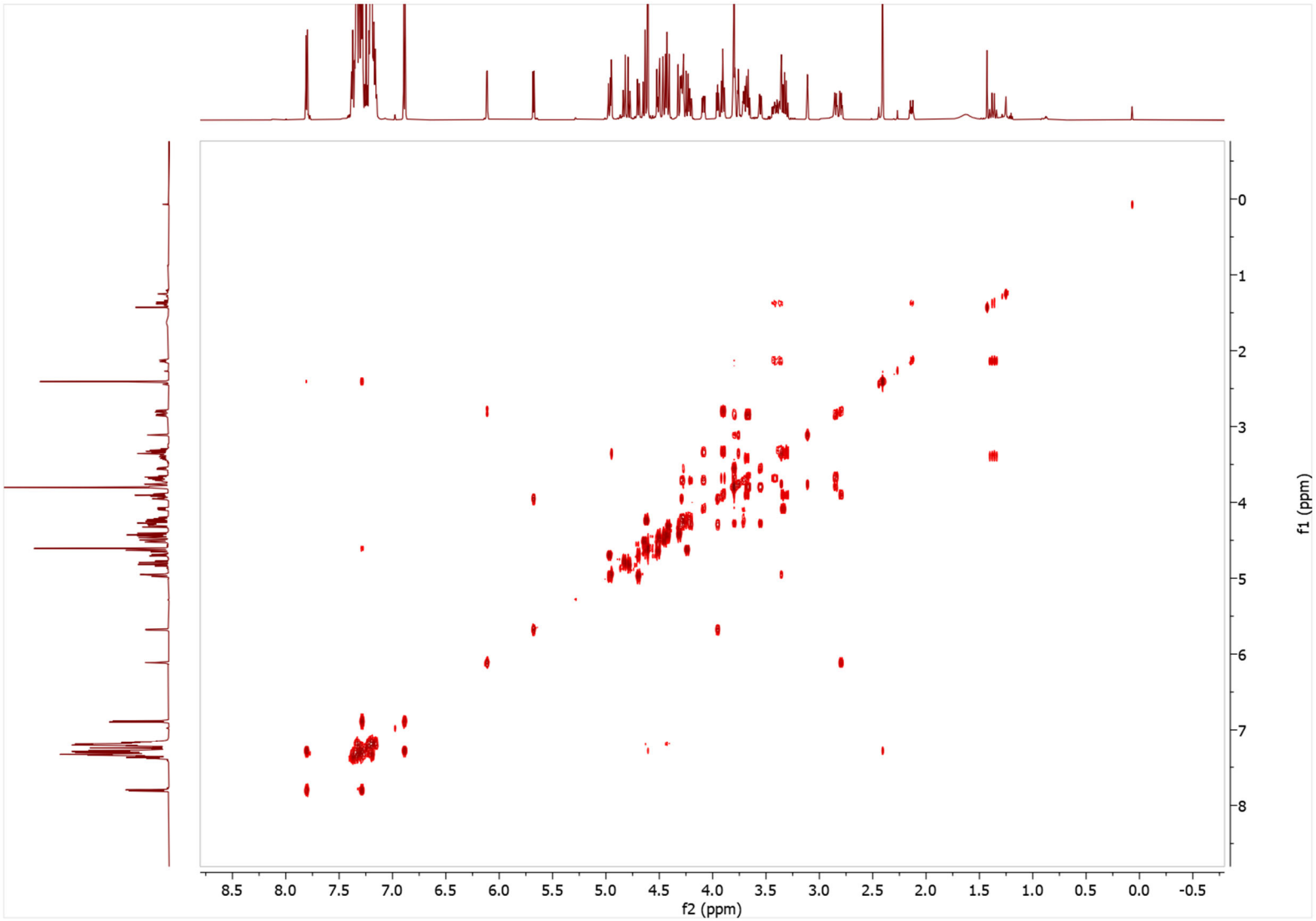
1,3,2’,2’’’,6’’’-Pentaazido-6,3’,6’,2’’,5’’,3’’’,4’’’-hepta-*O*-benzyl-1,3,2’,2’’’,6’’’-6’-*p*-toluenesulfonyloxymethyl-pentadeaminoparomomycin (14(*R*)) ^{1}H NMR (600 MHz, $CDCl_3$)



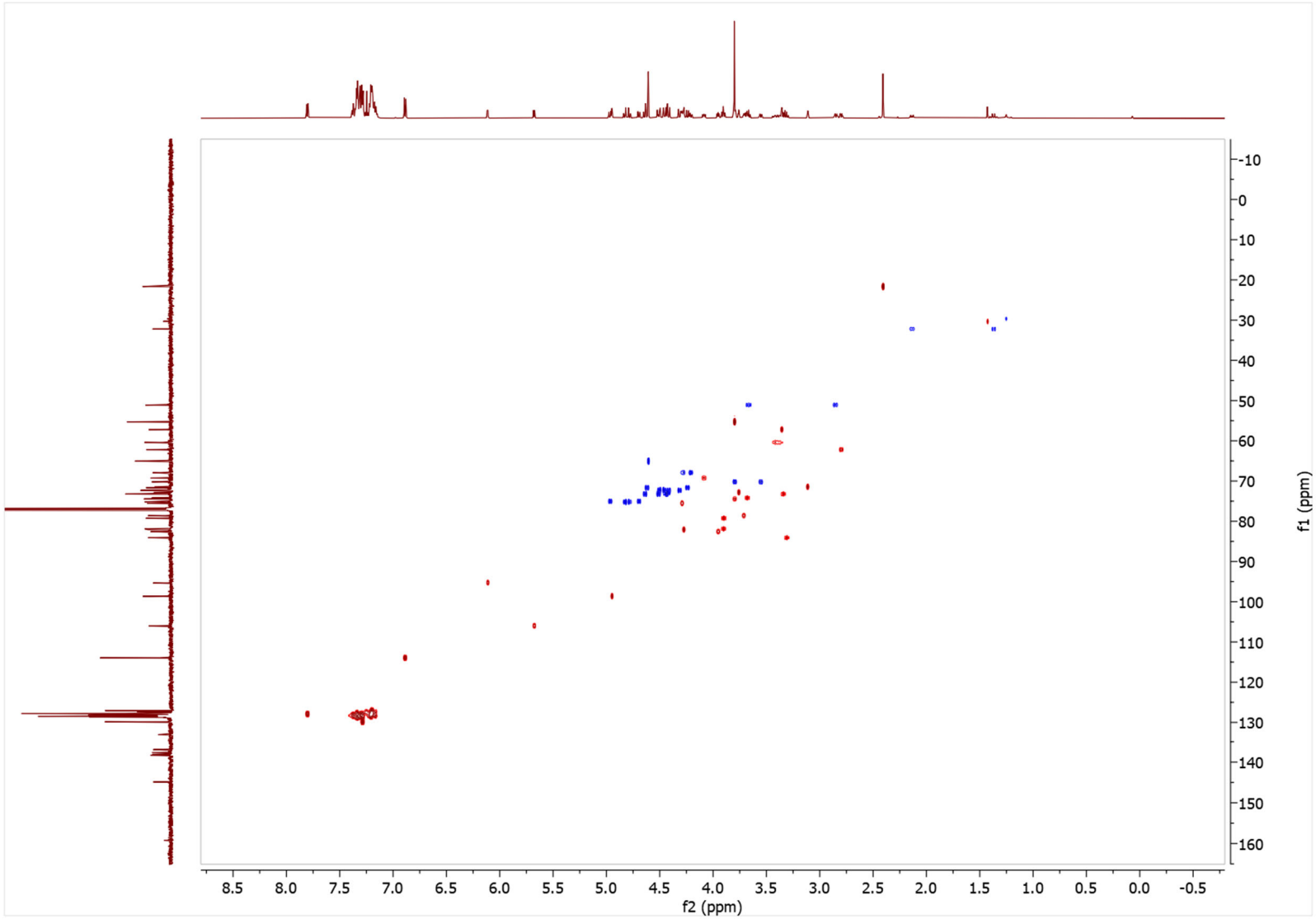
1,3,2’,2’’’,6’’’-Pentaazido-6,3’,6’,2’’,5’’,3’’’,4’’’-hepta-*O*-benzyl-1,3,2’,2’’’,6’’’-6’-*p*-toluenesulfonyloxymethyl-pentadeaminoparomomycin (14(*R*)) ^{13}C NMR (151 MHz, $CDCl_3$)



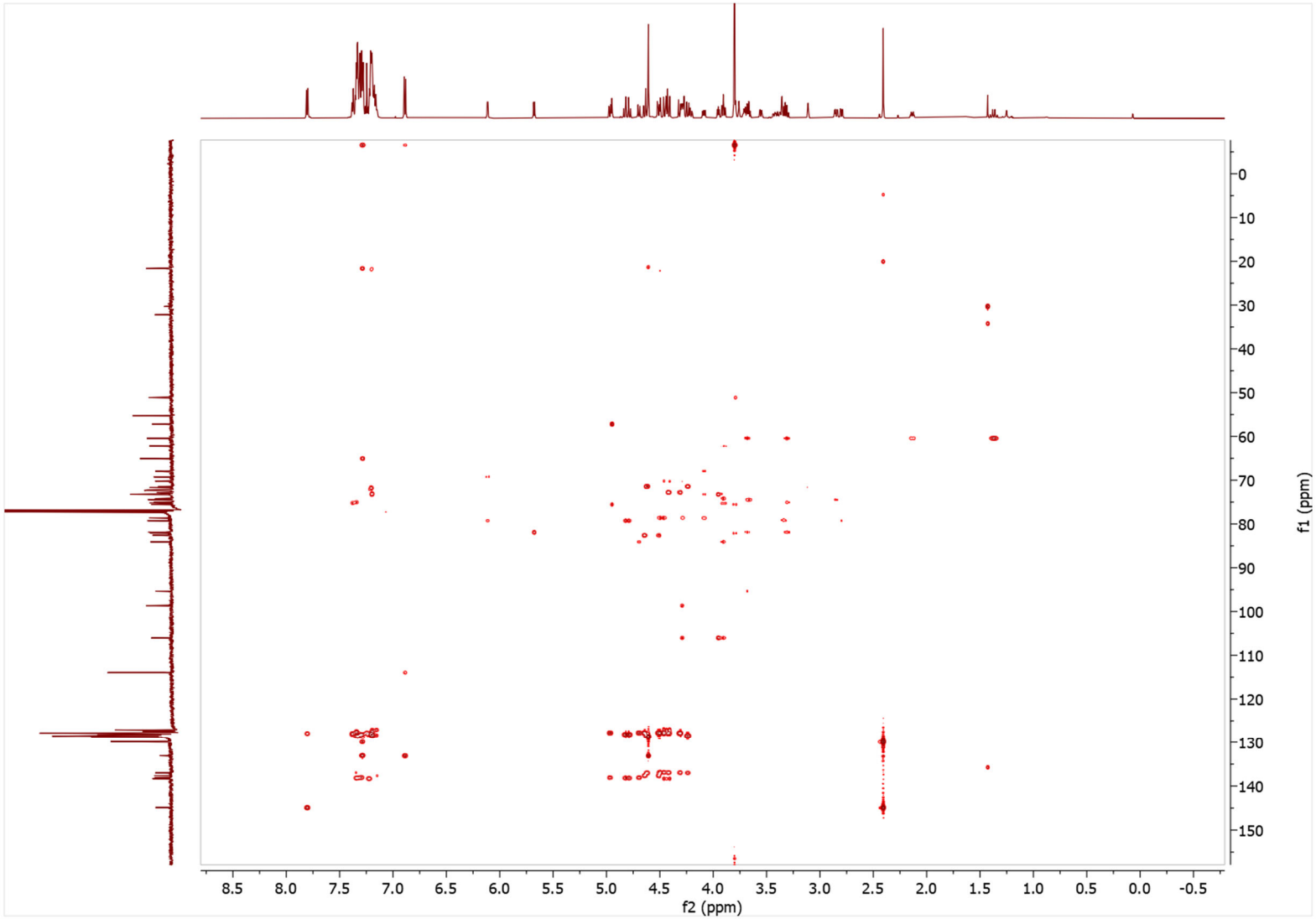
1,3,2’,2’’’,6’’’-Pentaazido-6,3’,6’,2’’,5’’,3’’’,4’’’-hepta-*O*-benzyl-1,3,2’,2’’’,6’’’-6’-*p*-toluenesulfonyloxymethyl-pentadeaminoparomomycin (14(*R*)) COSY



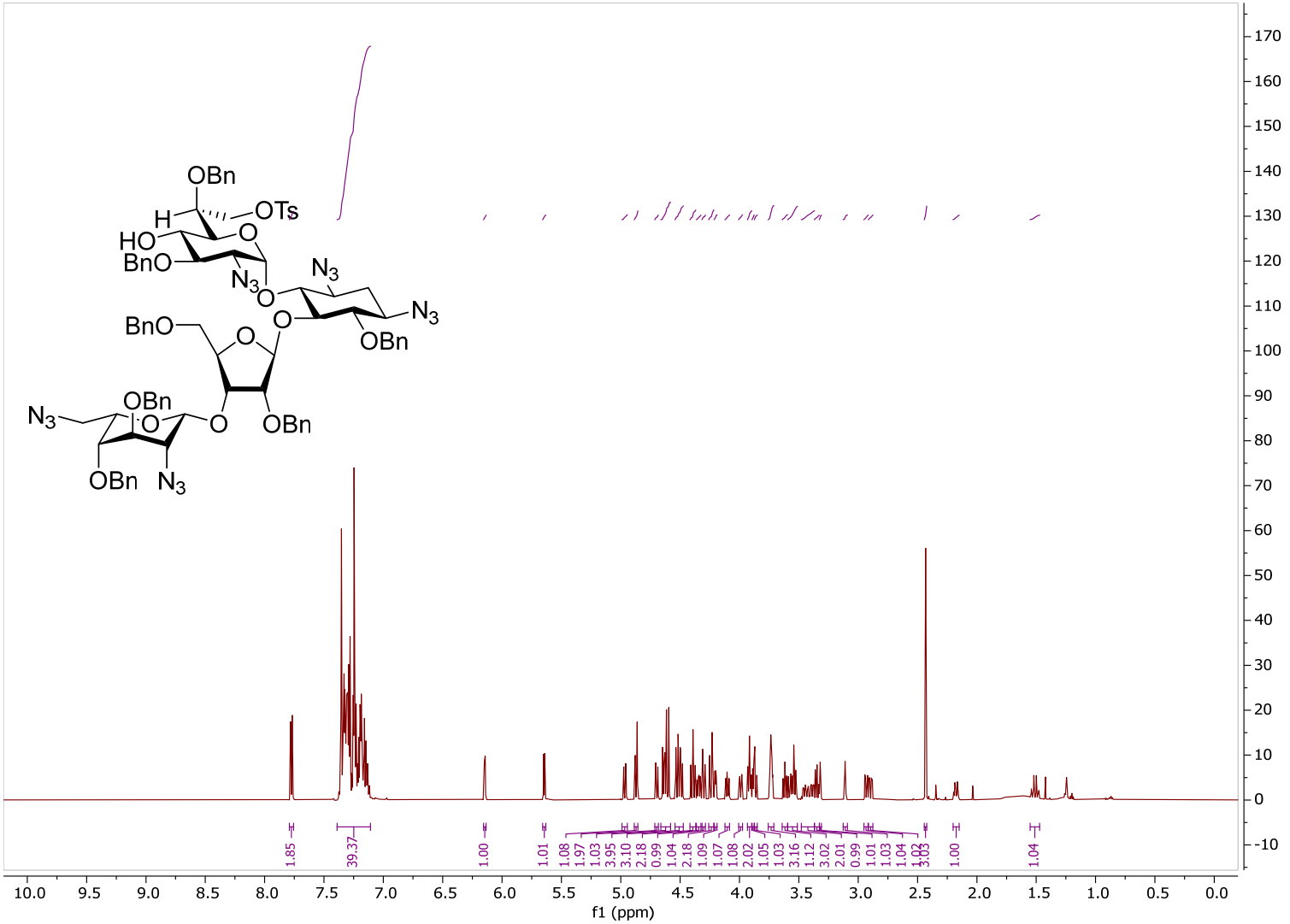
1,3,2’,2’’’,6’’’-Pentaazido-6,3’,6’,2’’,5’’,3’’’,4’’’-hepta-*O*-benzyl-1,3,2’,2’’’,6’’’-6’-*p*-toluenesulfonyloxymethyl-pentadeaminoparomomycin (14(*R*)) HSQC



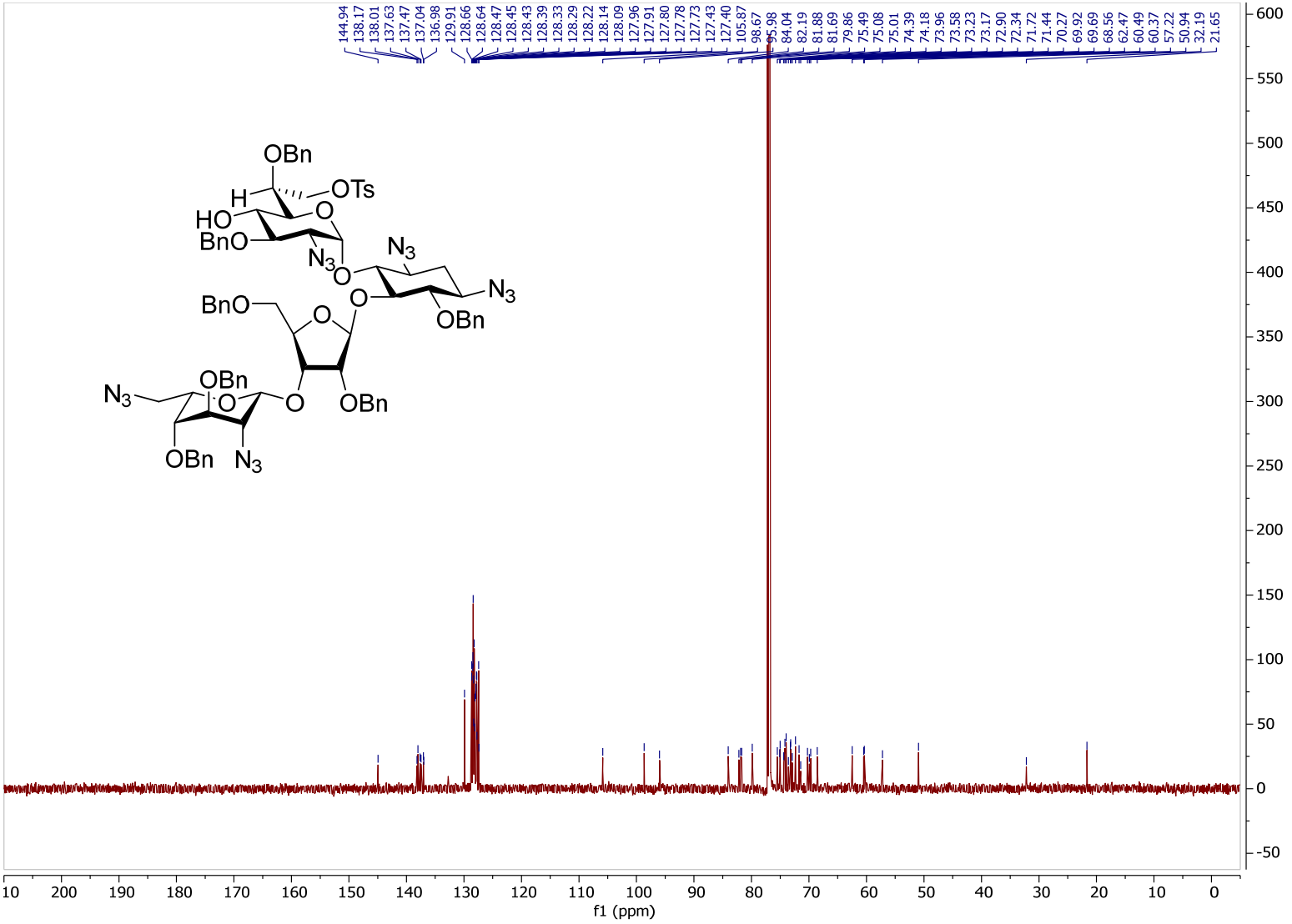
1,3,2’,2’’’,6’’’-Pentaazido-6,3’,6’,2’’,5’’,3’’’,4’’’-hepta-*O*-benzyl-1,3,2’,2’’’,6’’’-6’-*p*-toluenesulfonyloxymethyl-pentadeaminoparomomycin (14(*R*)) HMBC



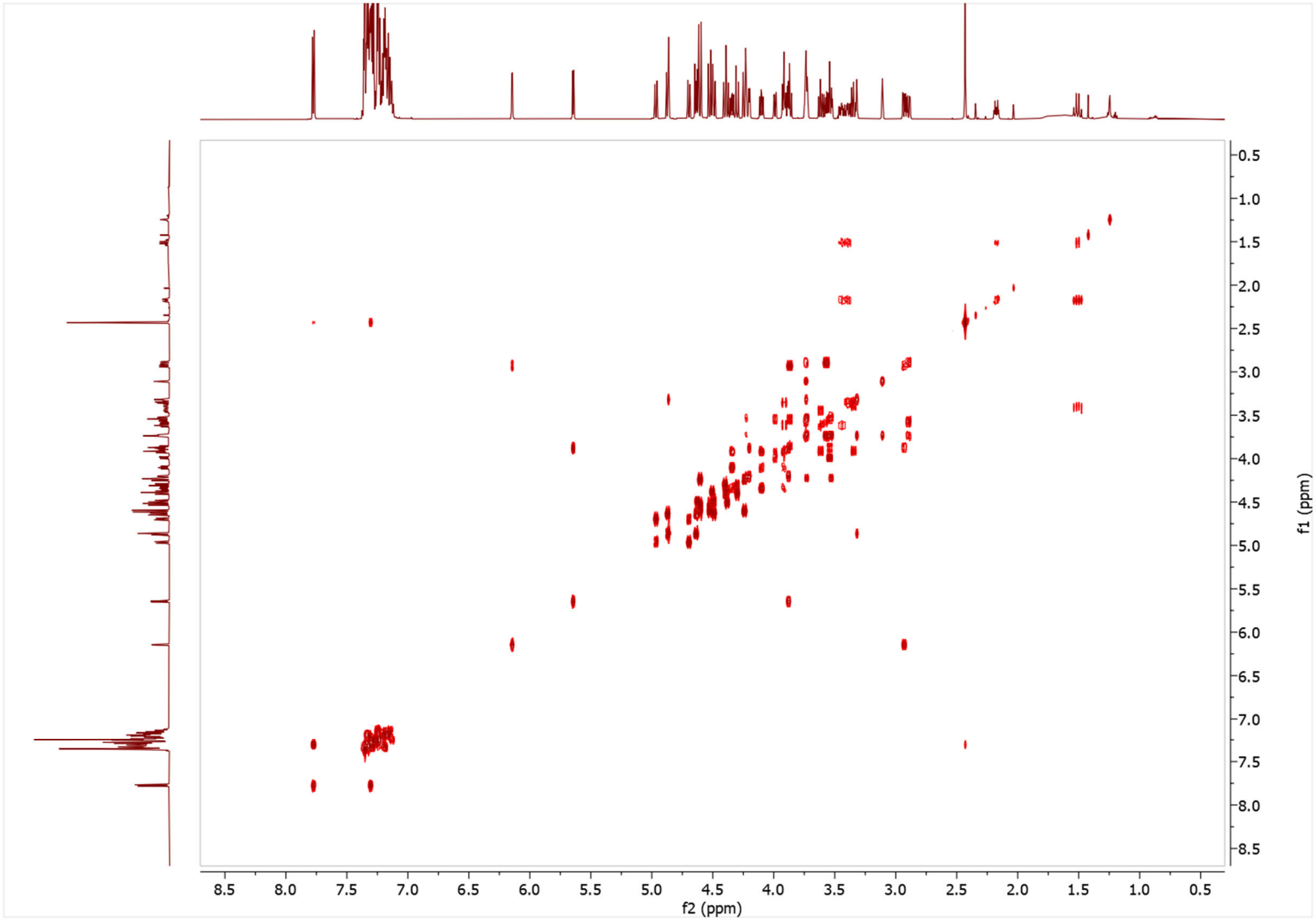
1,3,2’,2’’’,6’’’-Pentaazido-6,3’,6’,2’’,5’’,3’’’,4’’’-hepta-*O*-benzyl-1,3,2’,2’’’,6’’’-6’-*p*-toluenesulfonyloxymethyl-pentadeaminoparomomycin (14(*S*)) ^{1}H NMR (600 MHz, $CDCl_3$)



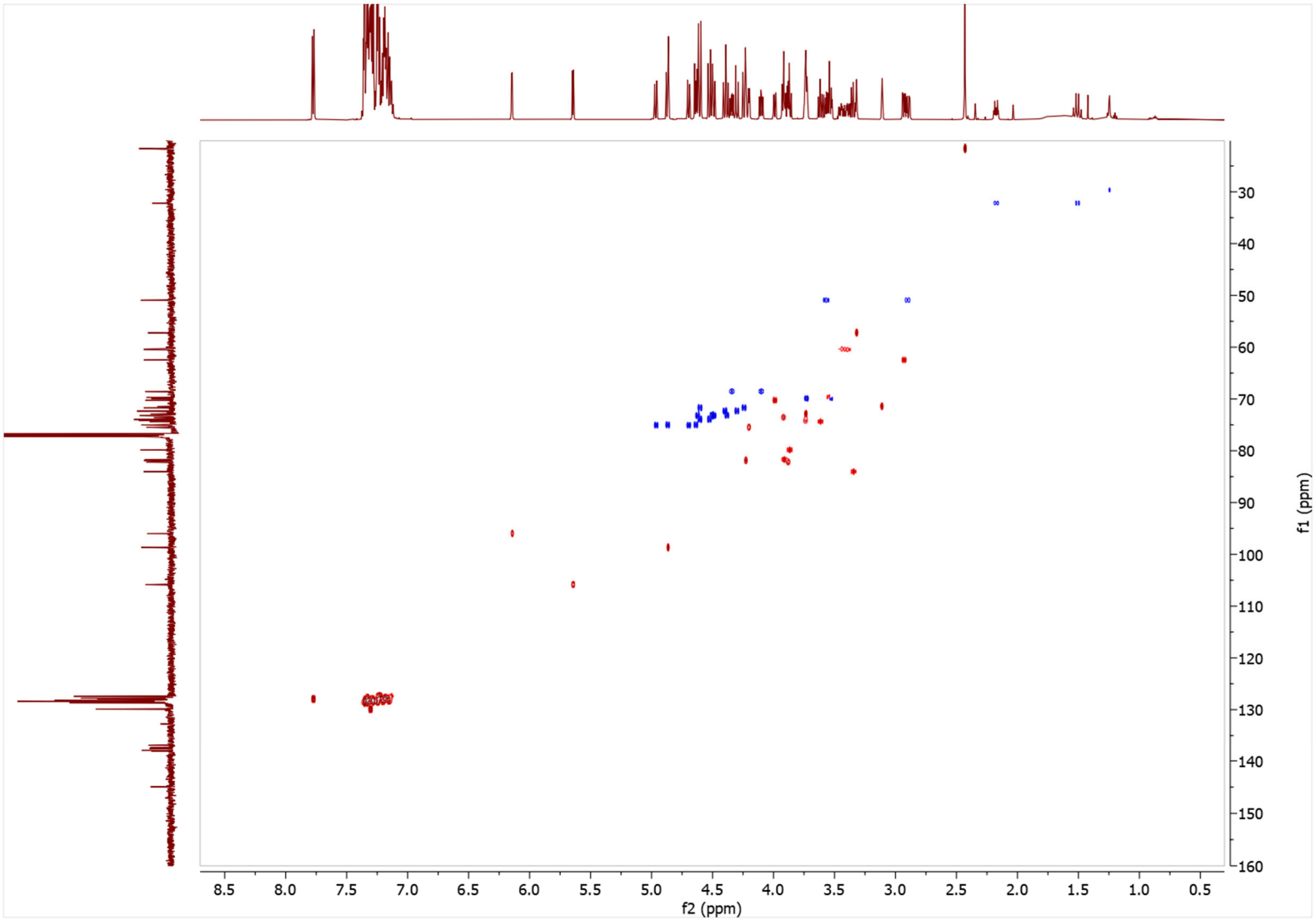
1,3,2',2''',6'''-Pentaazido-6,3',6',2'',5'',3''',4'''-hepta-*O*-benzyl-1,3,2',2''',6'''-6'-*p*-toluenesulfonyloxymethyl-pentadeaminoparomomycin (14(*S*)) ^{13}C NMR (151 MHz, $CDCl_3$)



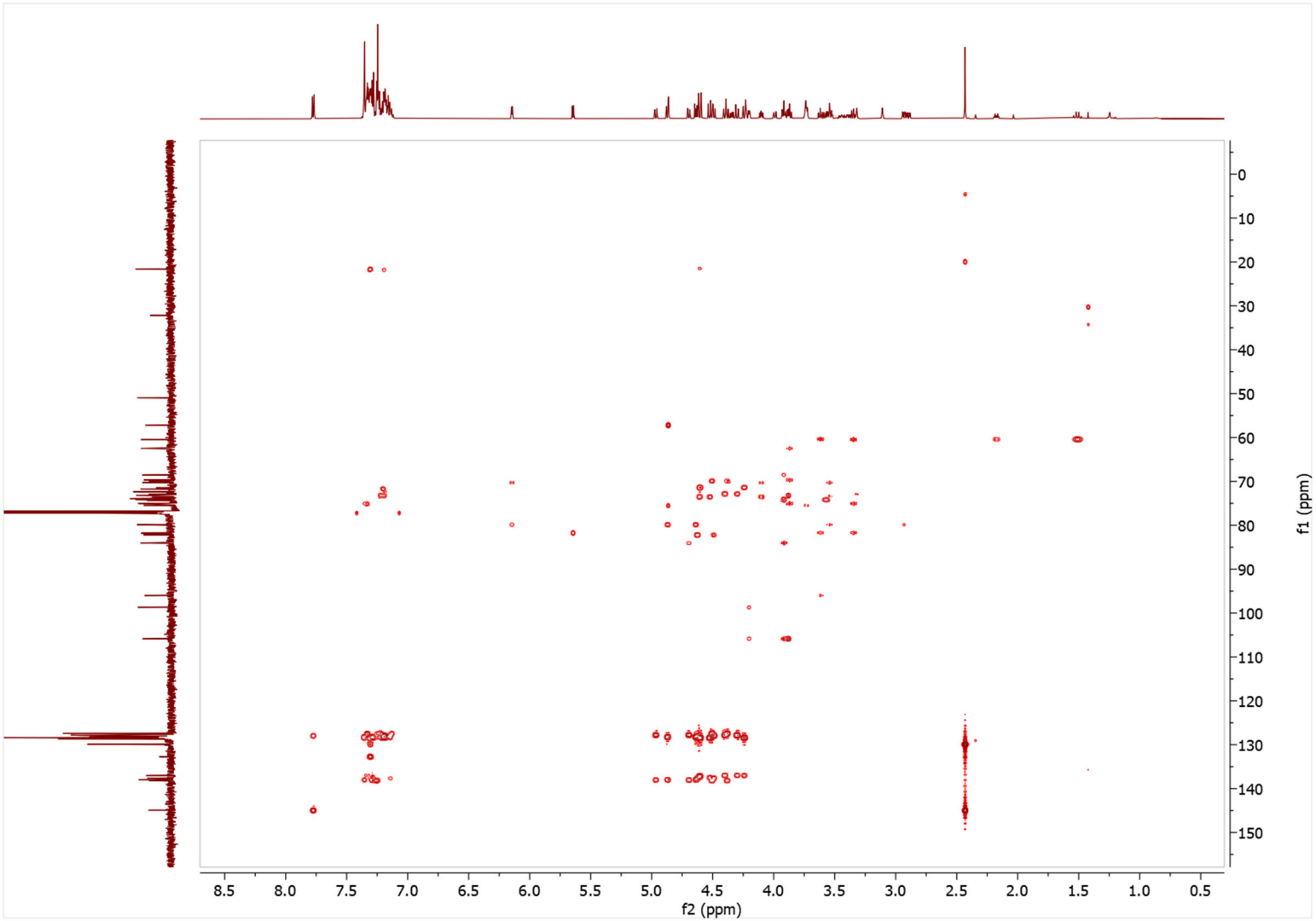
1,3,2’,2’’’,6’’’-Pentaazido-6,3’,6’,2’’,5’’,3’’’,4’’’-hepta-*O*-benzyl-1,3,2’,2’’’,6’’’-6’-*p*-toluenesulfonyloxymethyl-pentadeaminoparomomycin (14(*S*)) COSY



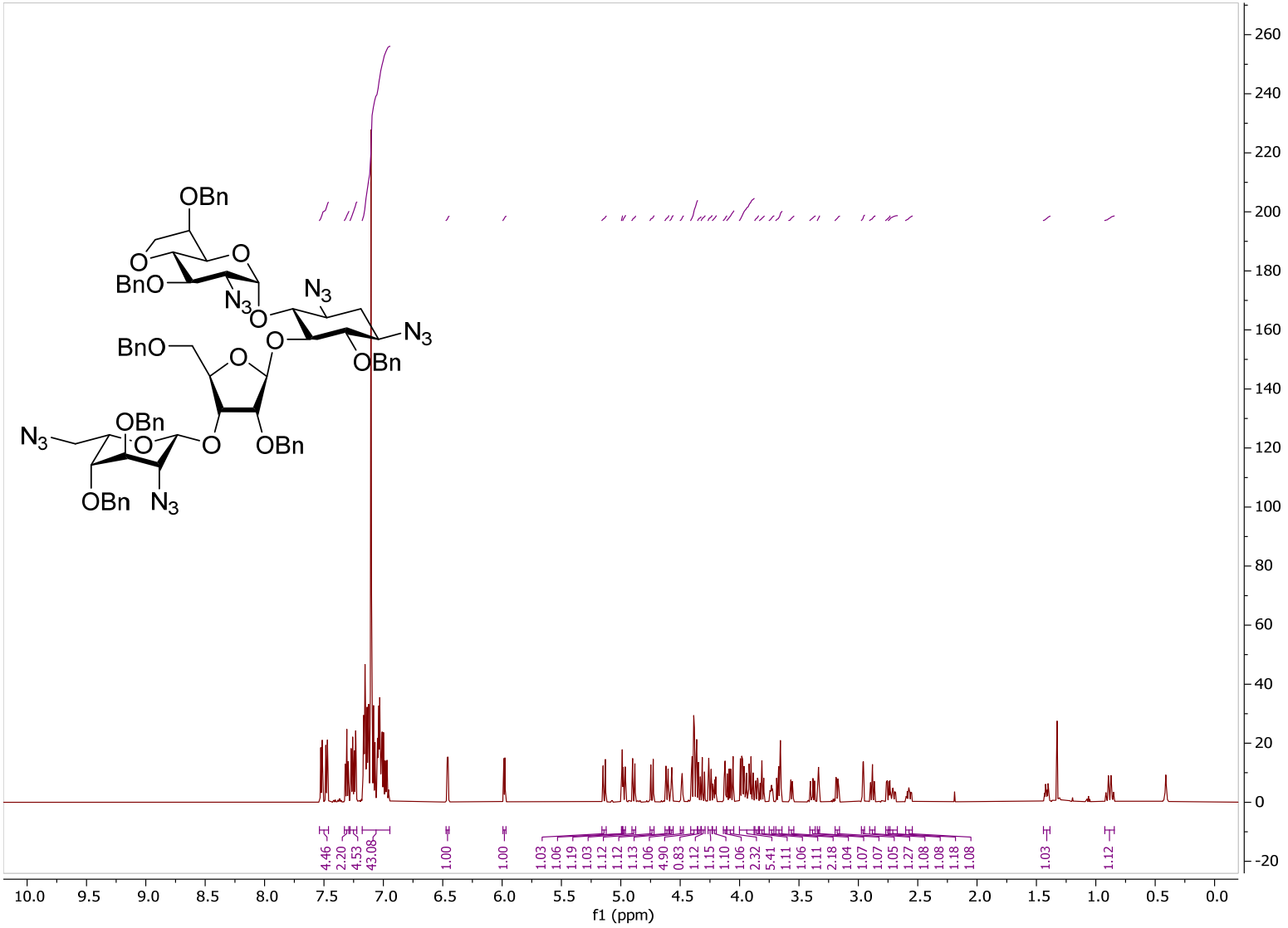
1,3,2’,2’’’,6’’’-Pentaazido-6,3’,6’,2’’,5’’,3’’’,4’’’-hepta-*O*-benzyl-1,3,2’,2’’’,6’’’-6’-*p*-toluenesulfonyloxymethyl-pentadeaminoparomomycin (14(*S*)) HSQC



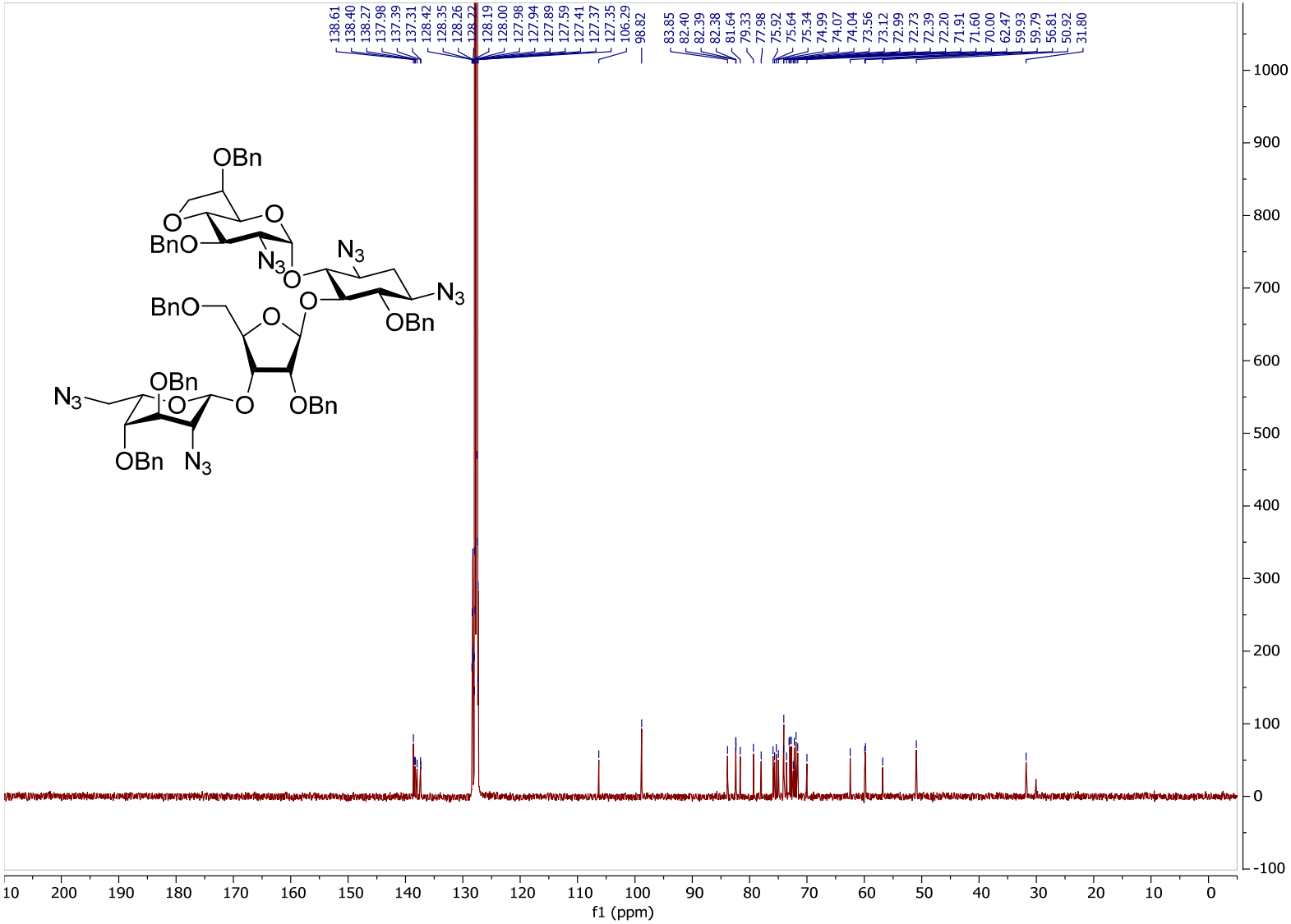
1,3,2’,2’’’,6’’’-Pentaazido-6,3’,6’,2’’,5’’,3’’’,4’’’-hepta-*O*-benzyl-1,3,2’,2’’’,6’’’-6’-*p*-toluenesulfonyloxymethyl-pentadeaminoparomomycin (14(*S*)) HMBC



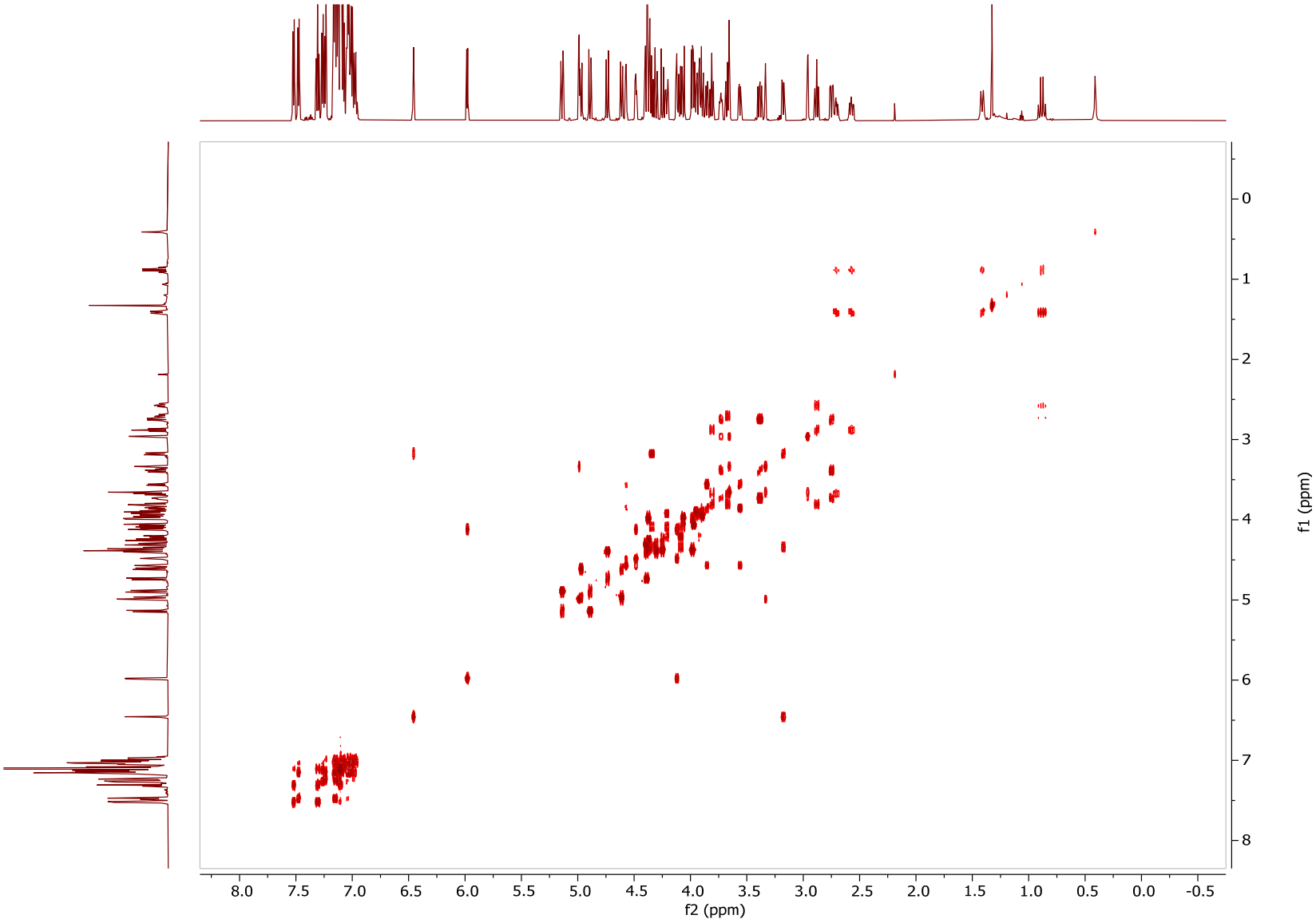
4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (15(ax)). ^{1}H NMR (600 MHz, C_6D_6)



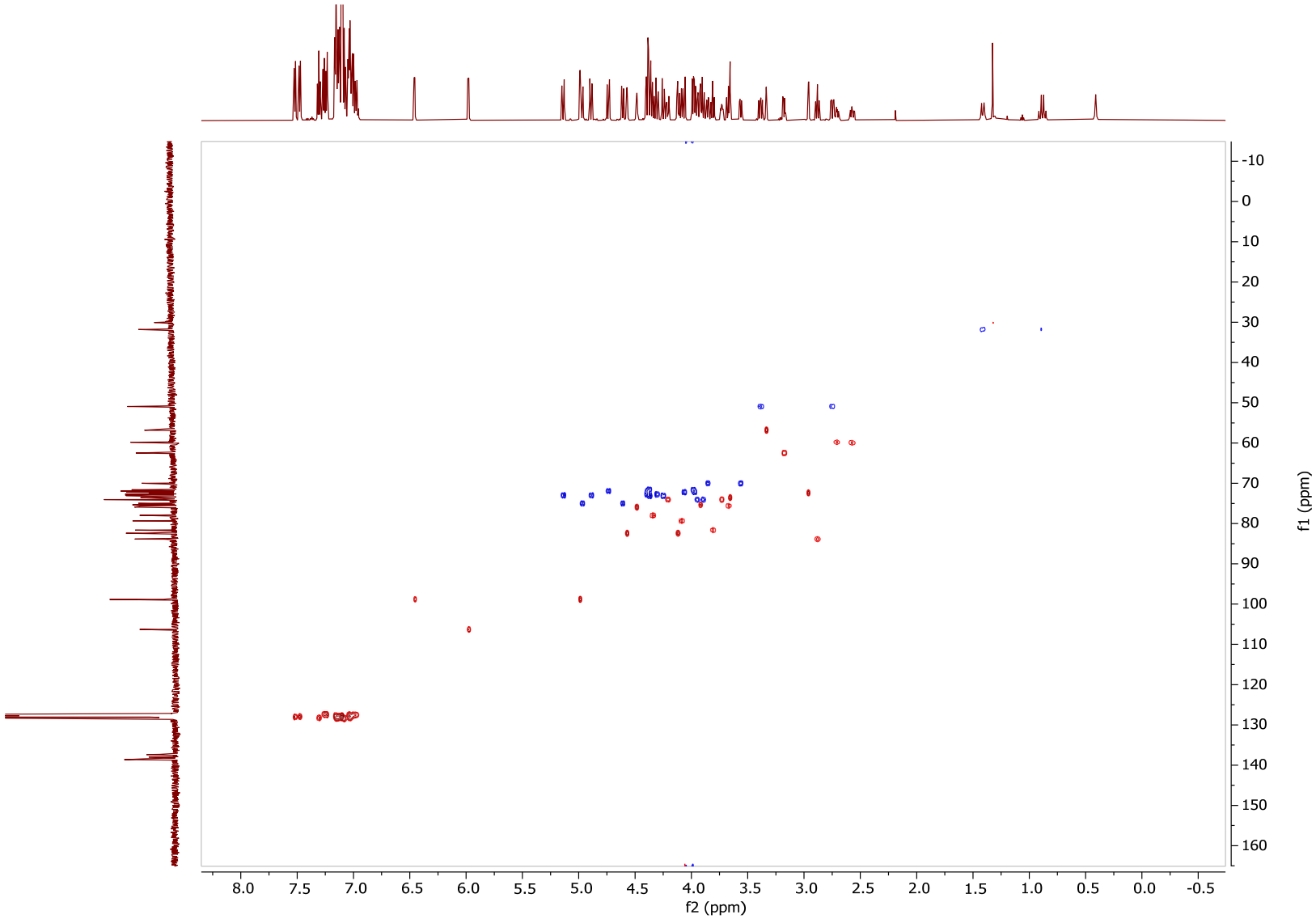
4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (15(ax)). ^{13}C NMR (151 MHz, C_6D_6)



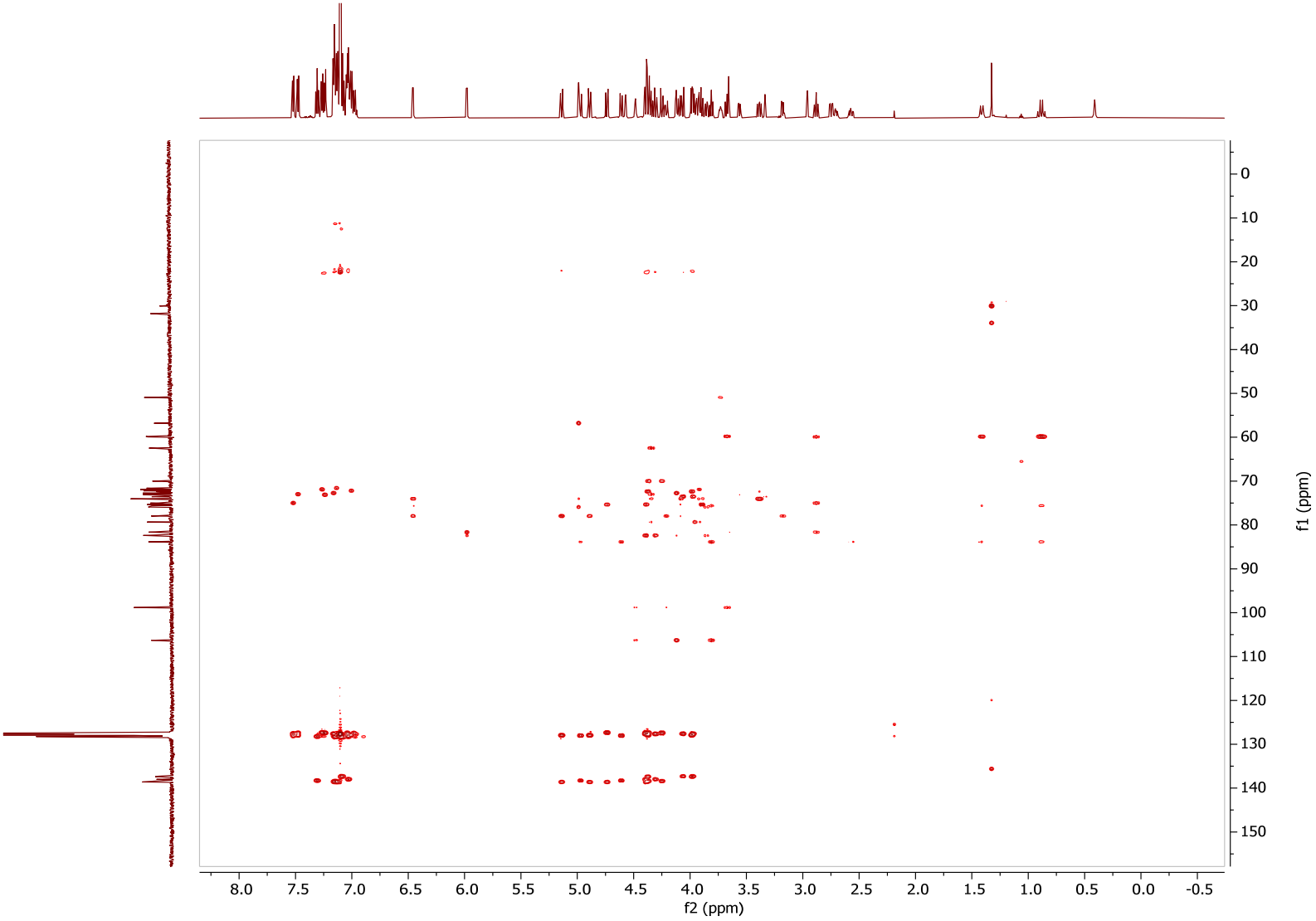
4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (15(ax)). COSY



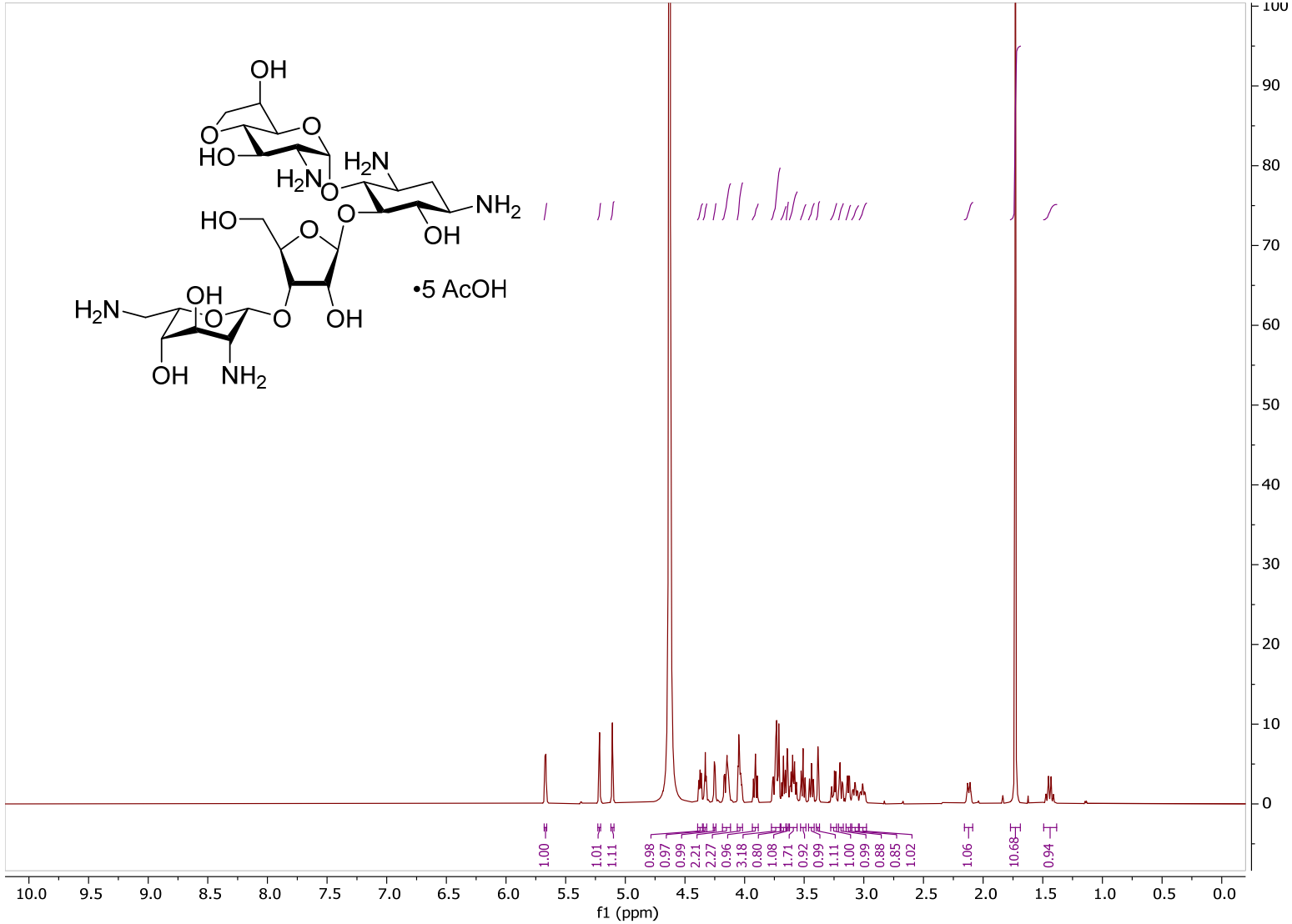
4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (15(ax)). HSQC



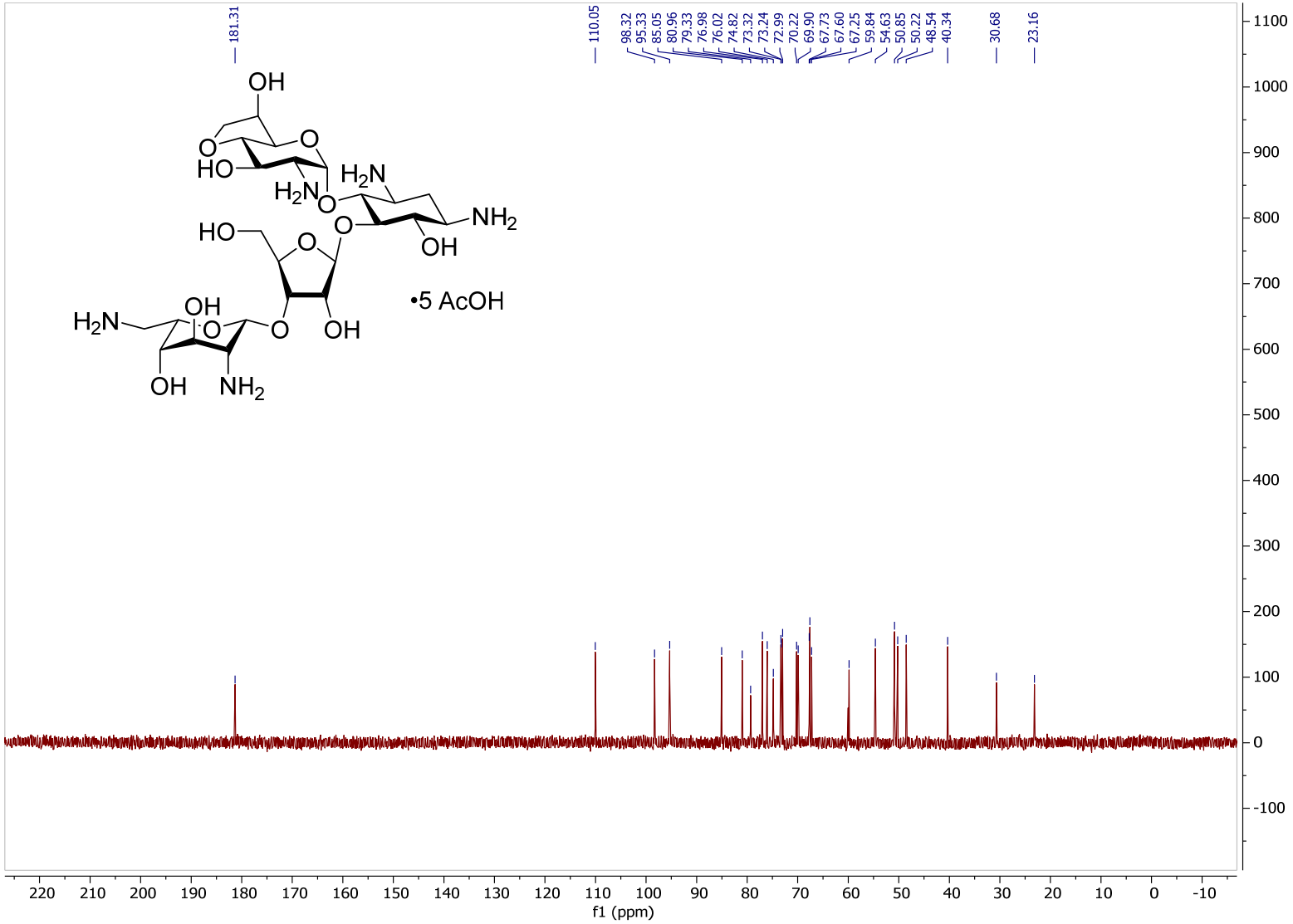
4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (15(ax)). HMBC



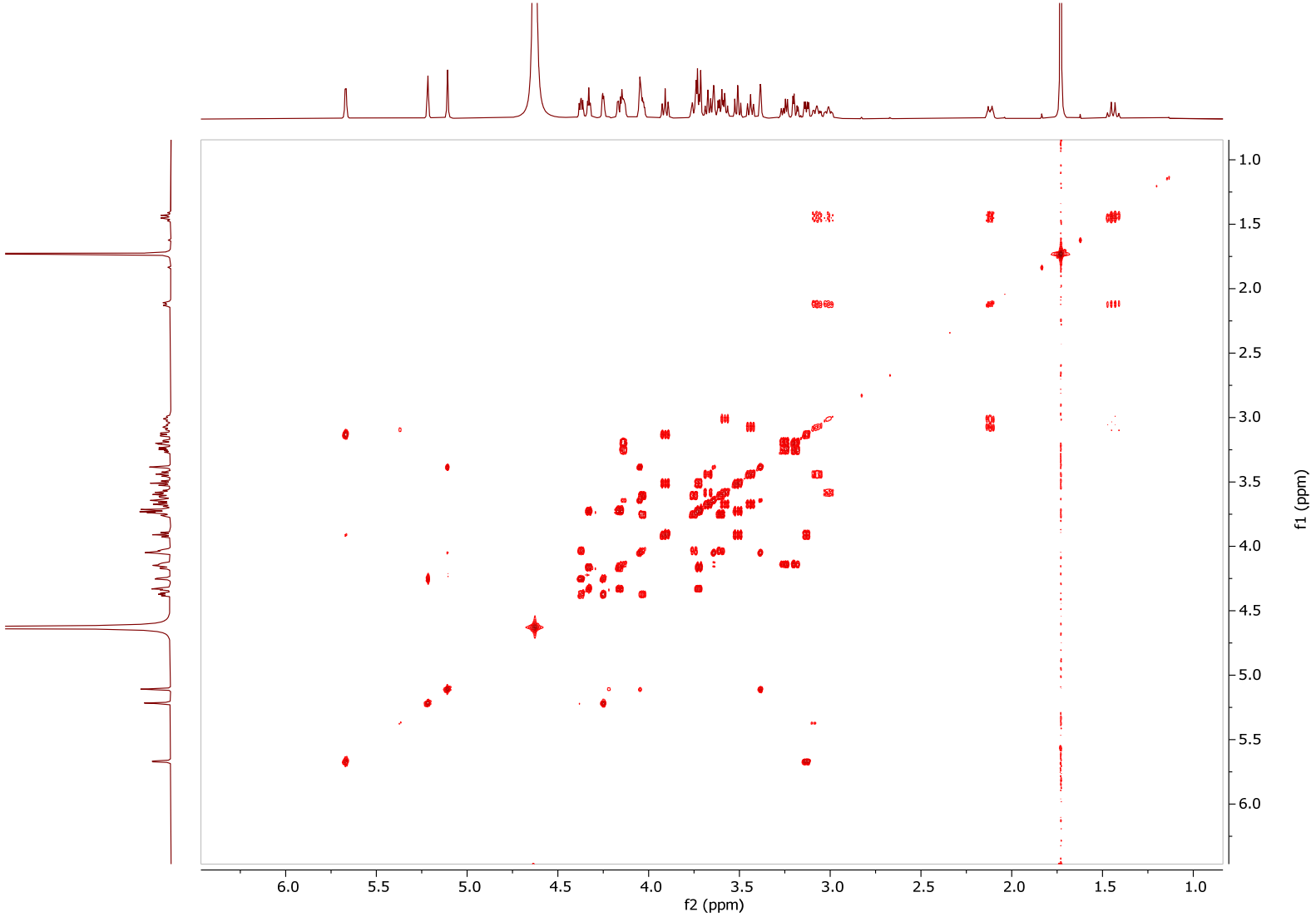
4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (7). ^{1}H NMR (600 MHz, D_2O)



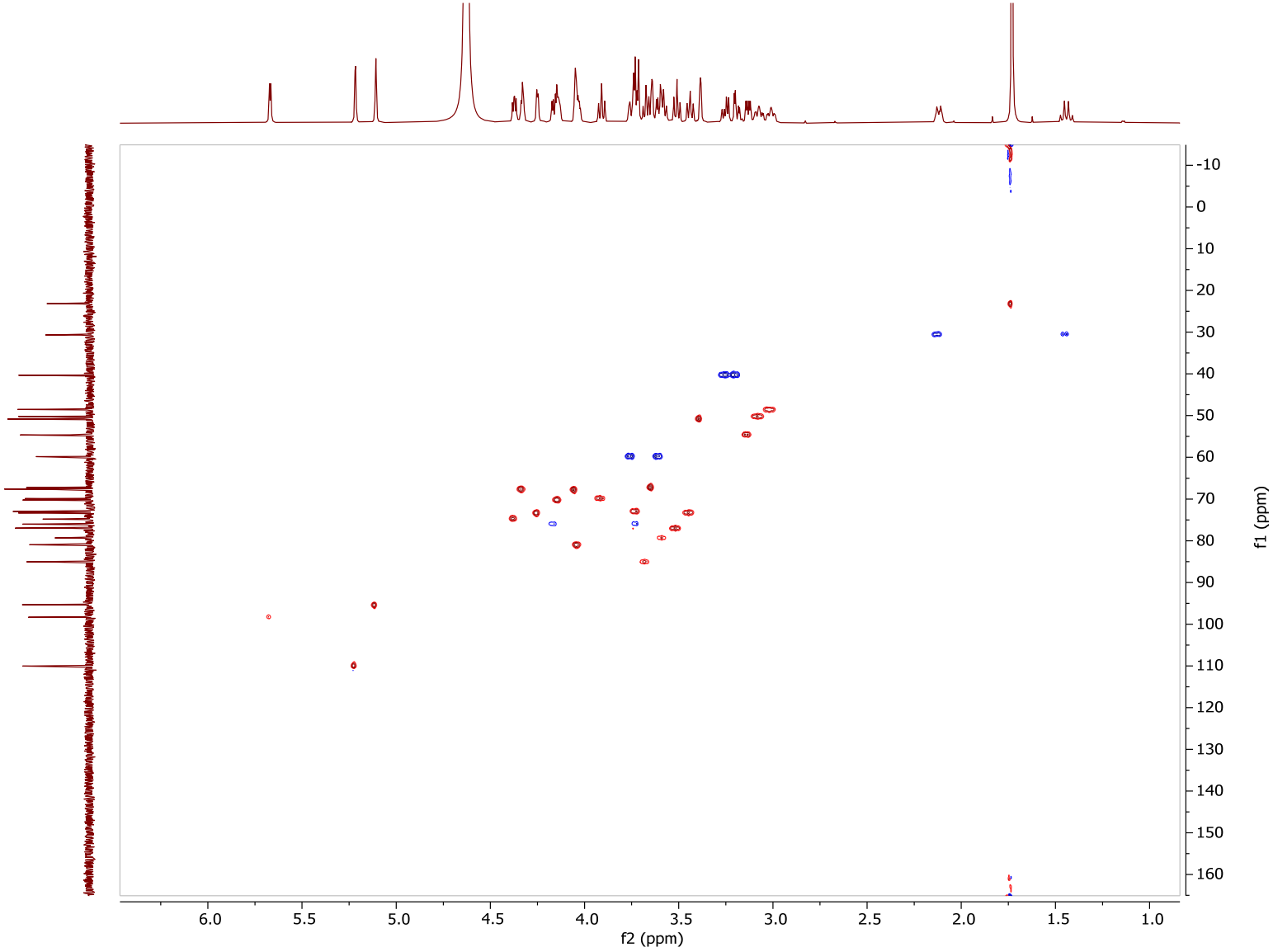
4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (7). ^{13}C NMR (151 MHz, D_2O)



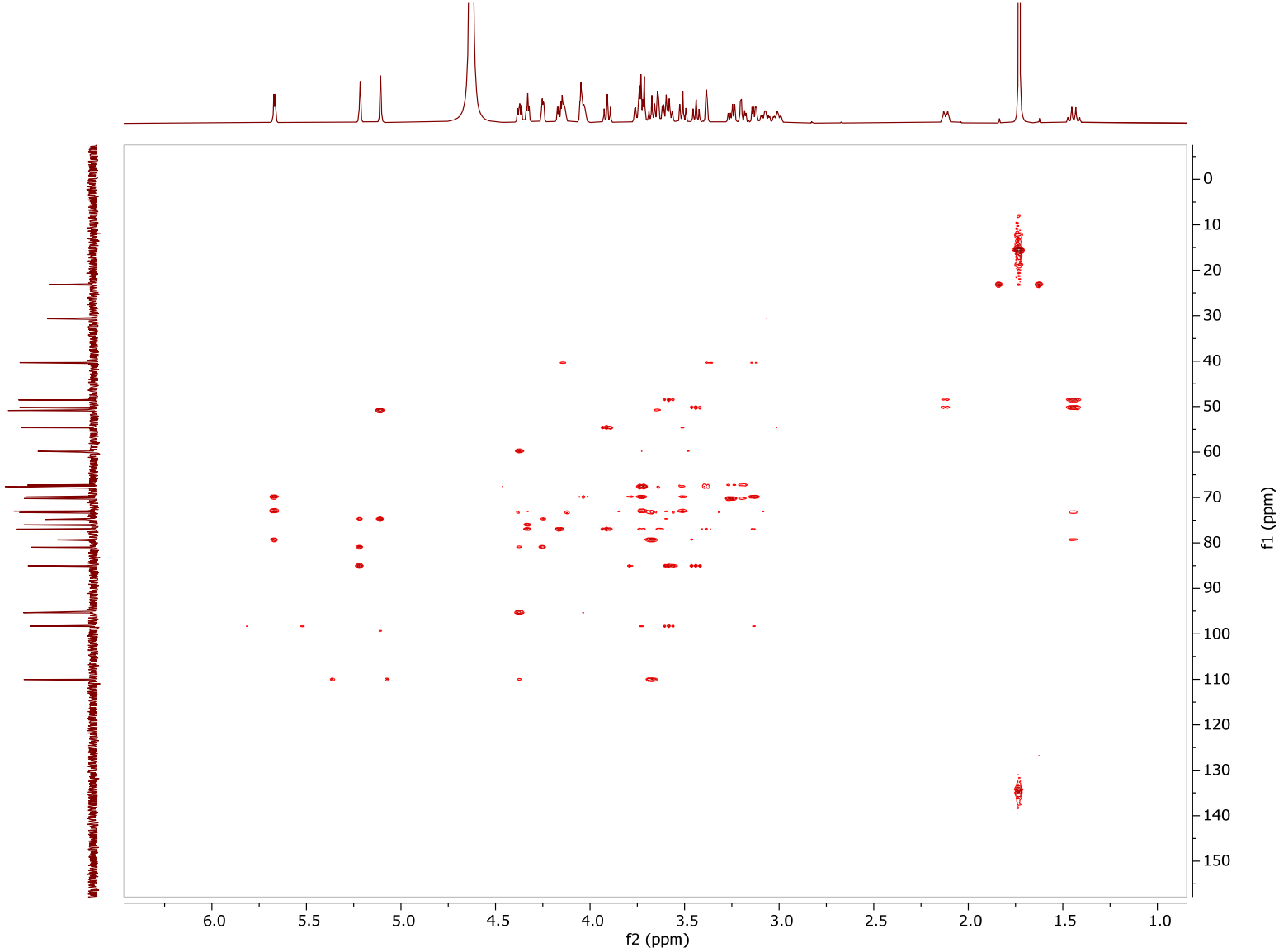
4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (7). COSY



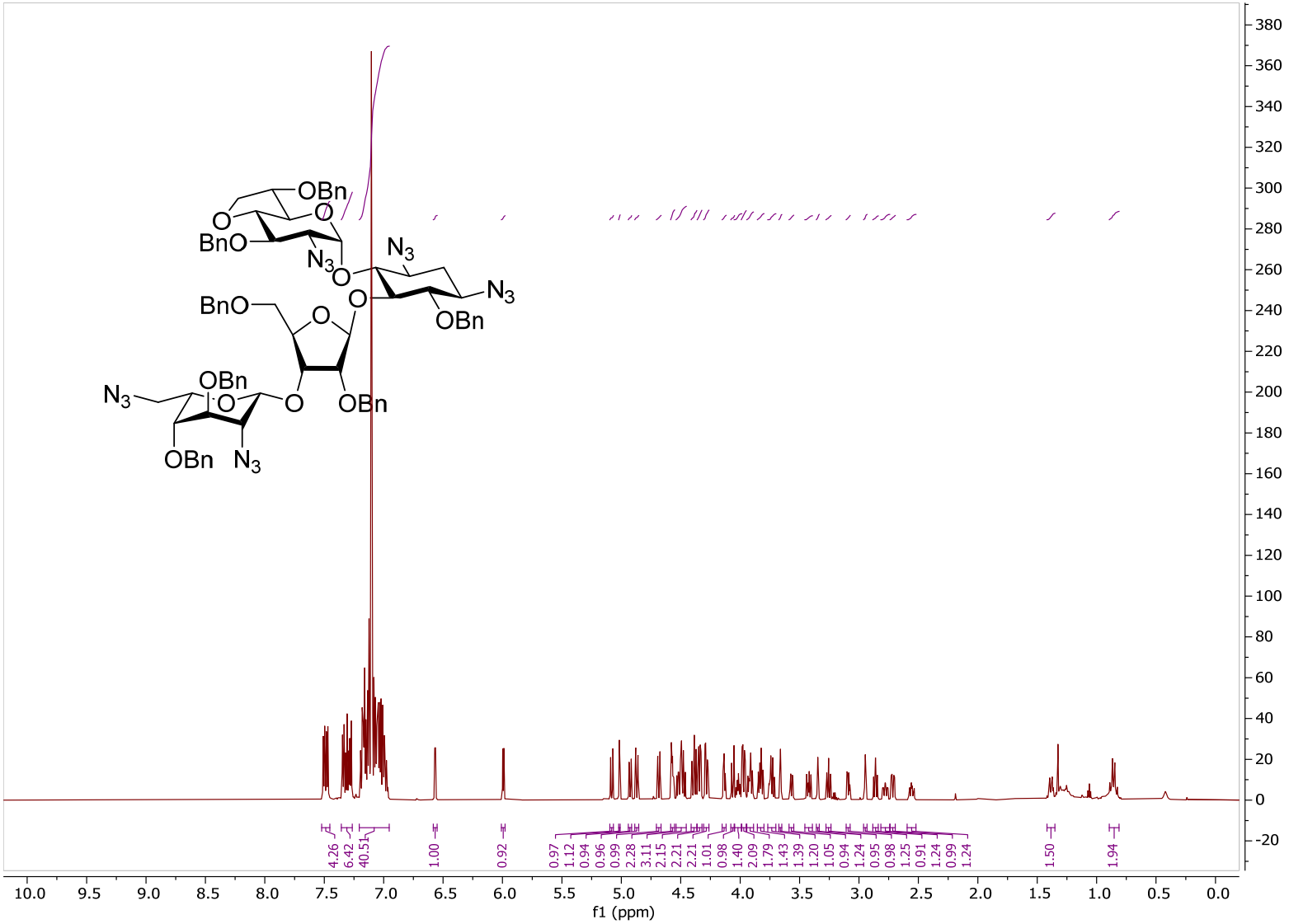
4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (7). HSQC



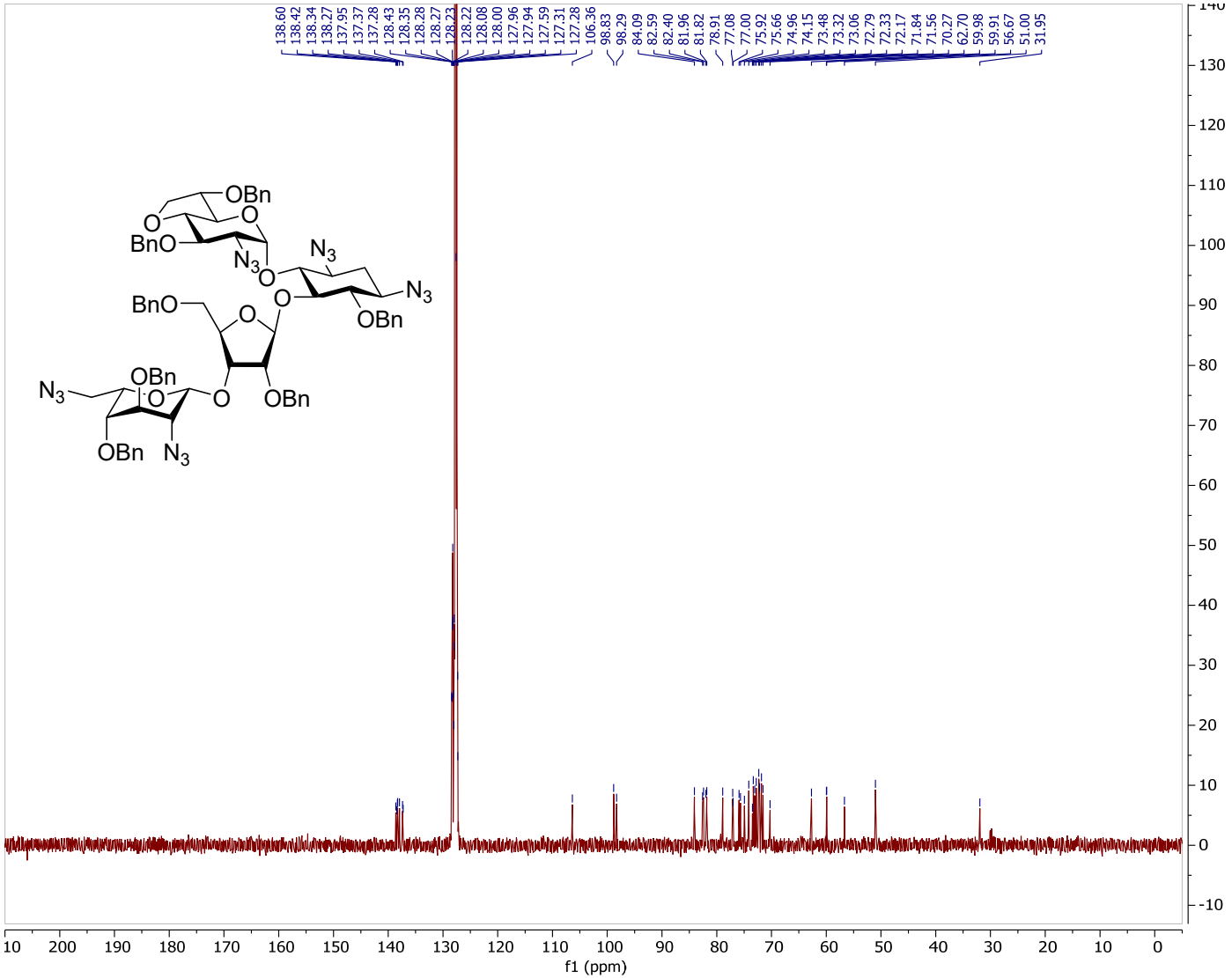
4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (7). HMBC



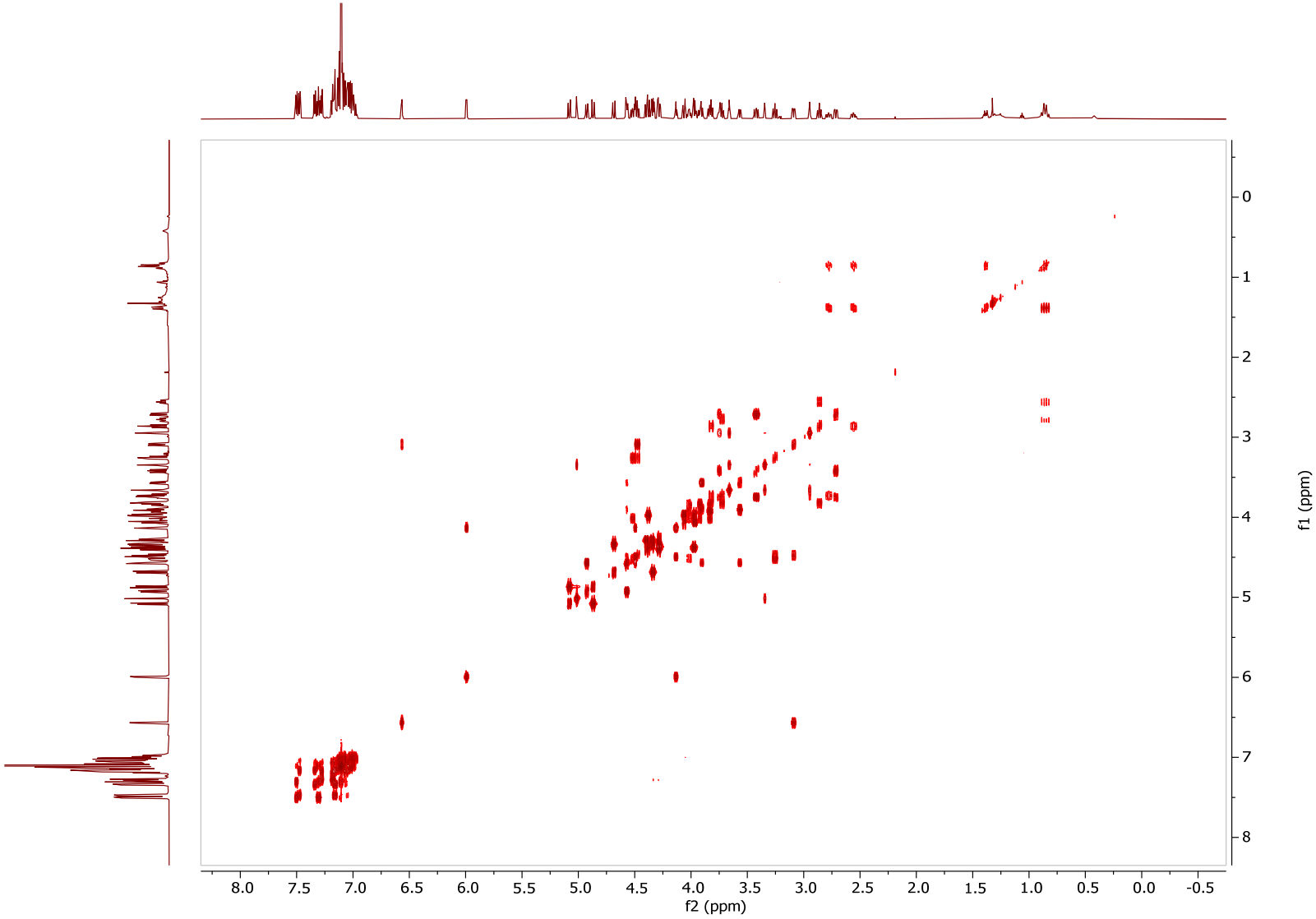
4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,7-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (15(eq)). ^{1}H NMR (600 MHz, C_6D_6)



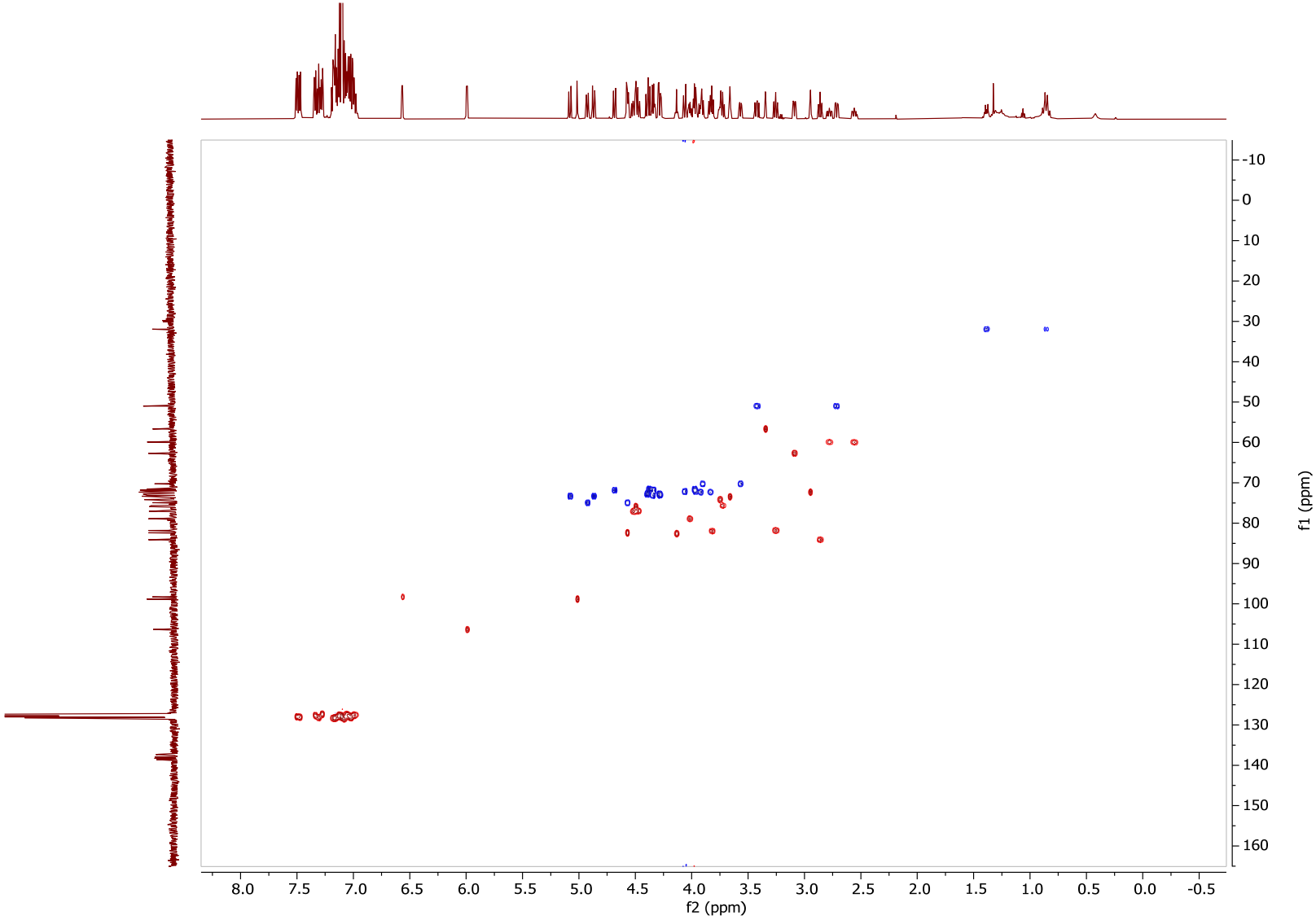
4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,7-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (15(eq)). ^{13}C NMR (151 MHz, C_6D_6)



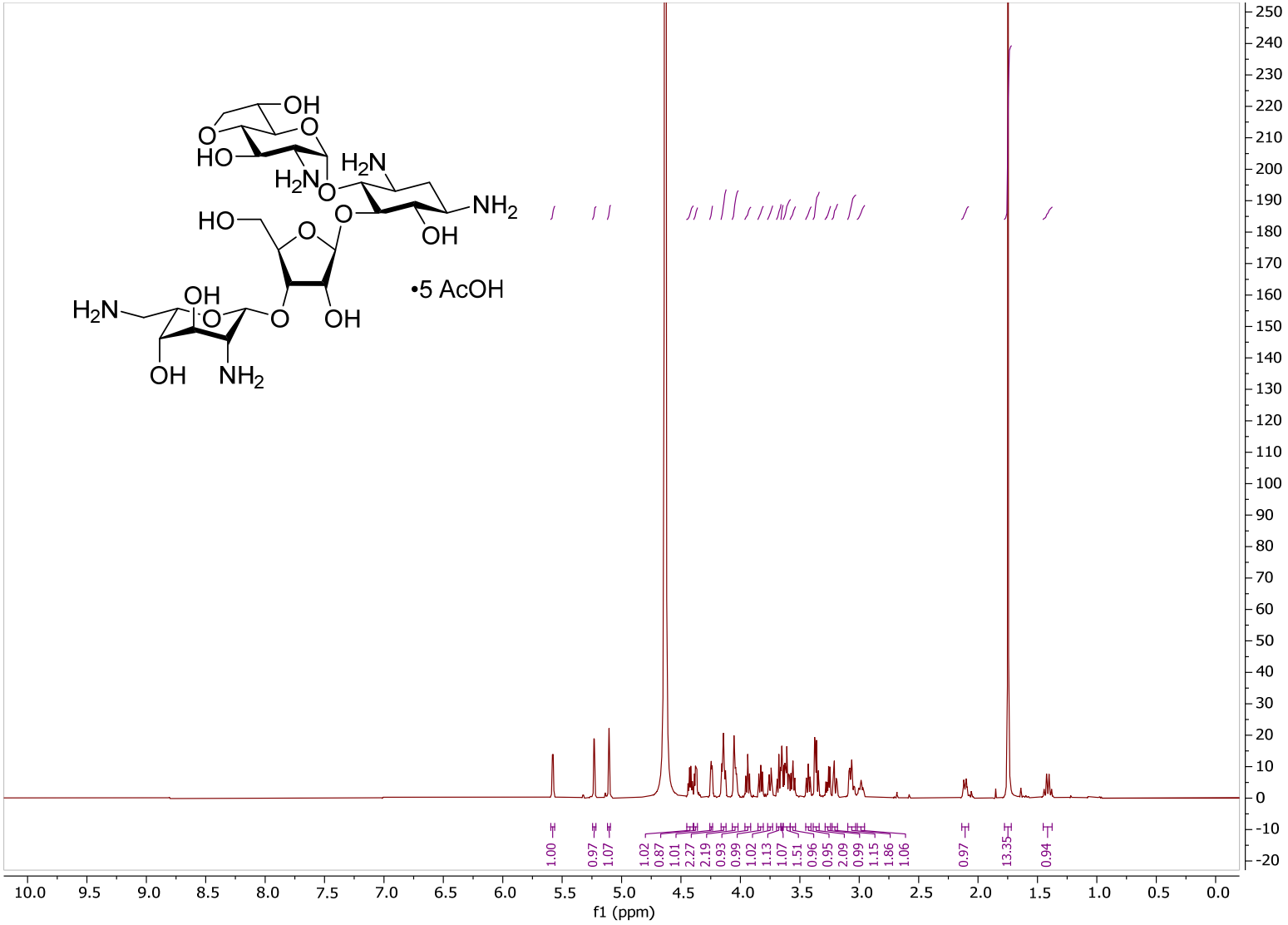
4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,7-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (15(eq)). COSY



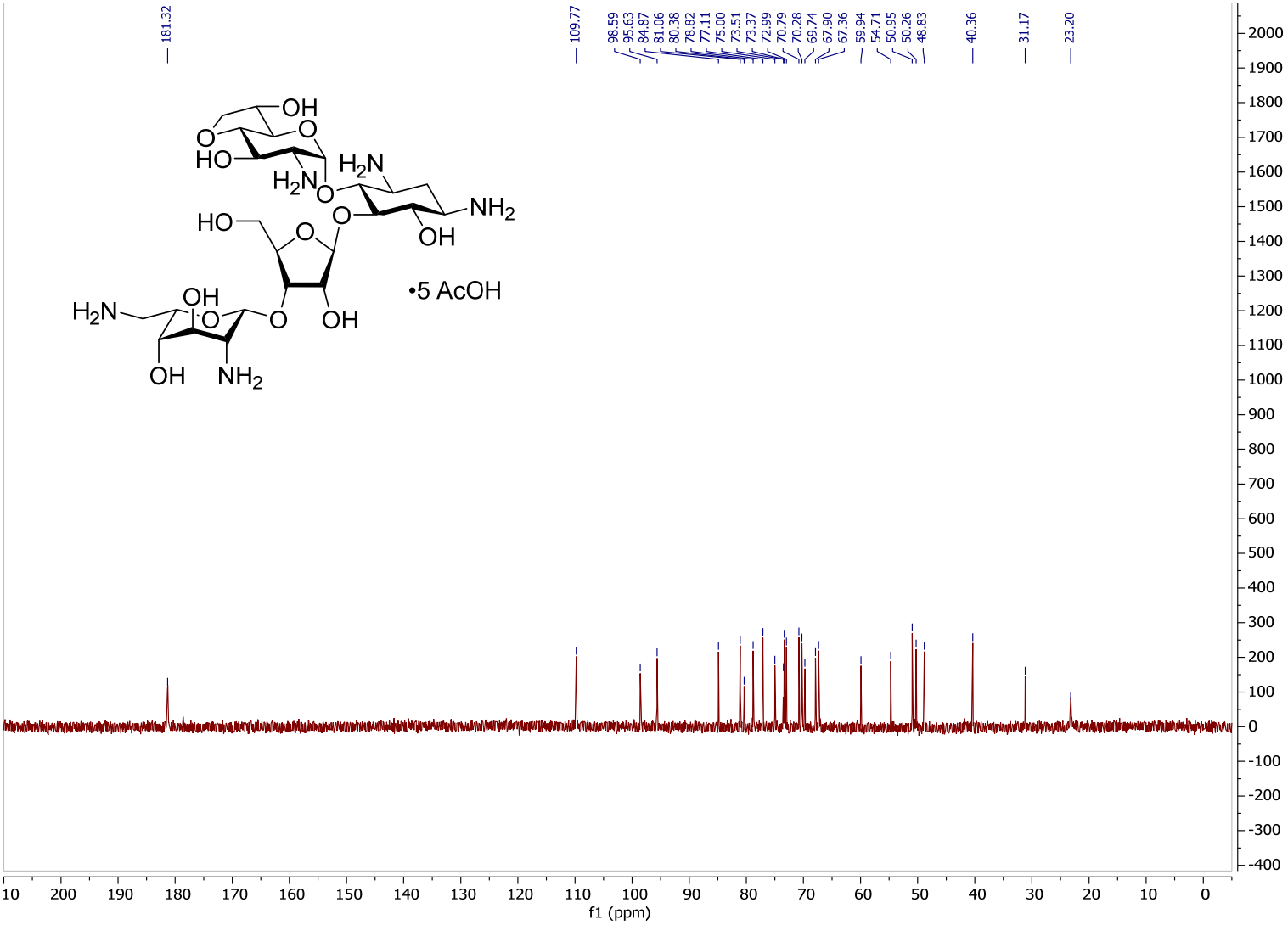
4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,7-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (15(eq)). HSQC



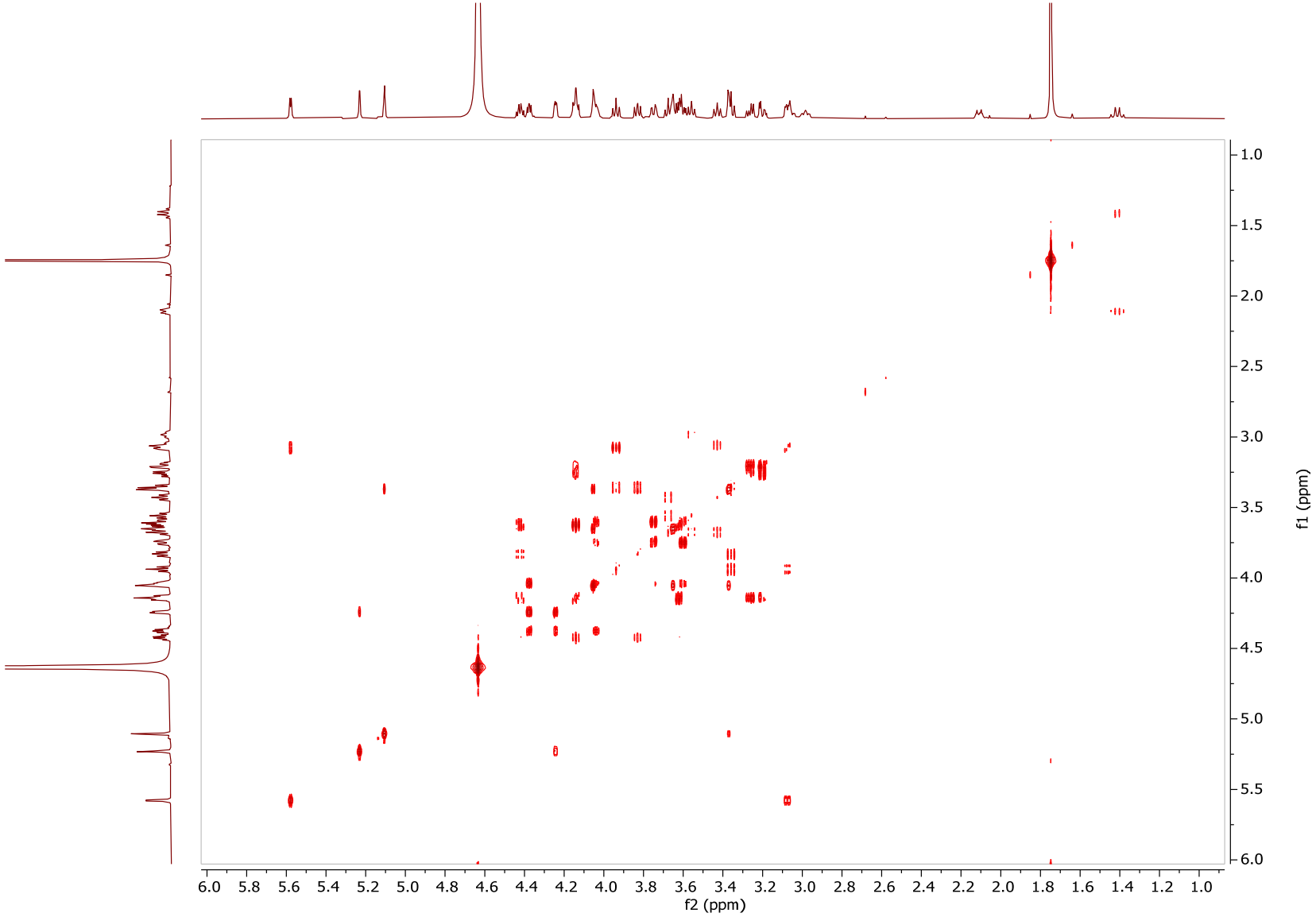
4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (6). ^{1}H NMR (600 MHz, D_2O)



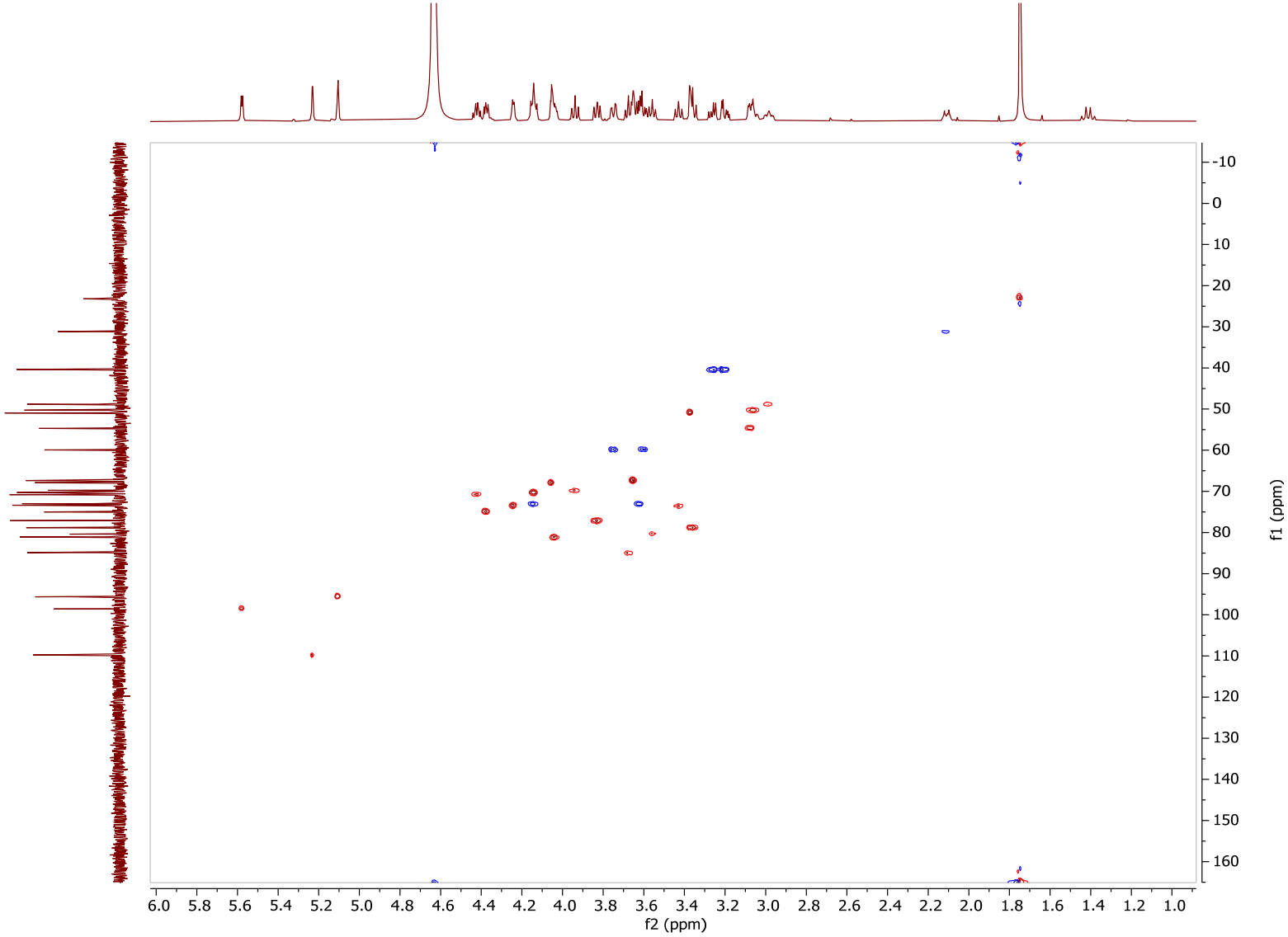
4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (6). ^{13}C NMR (151 MHz, D_2O)



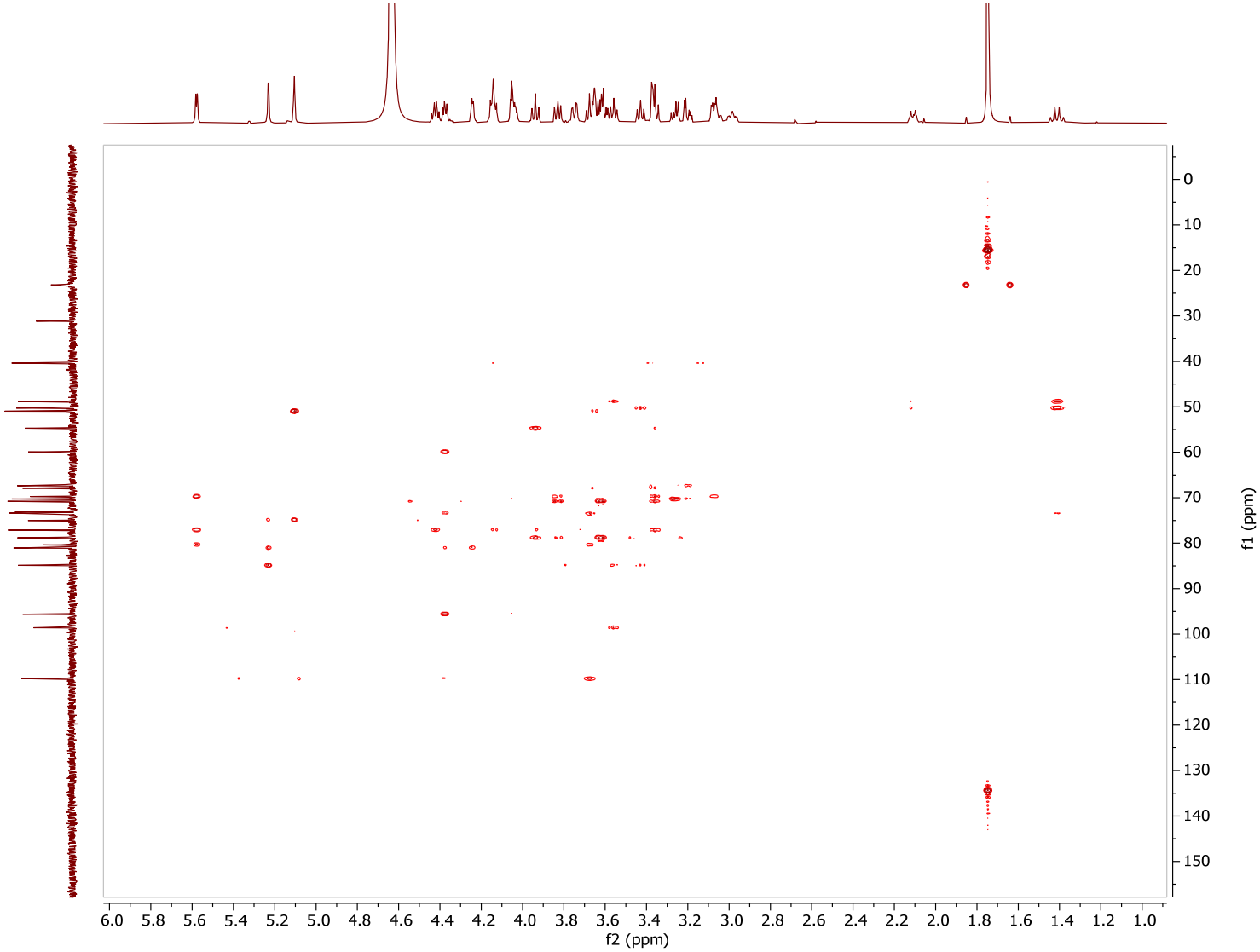
4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (6). COSY



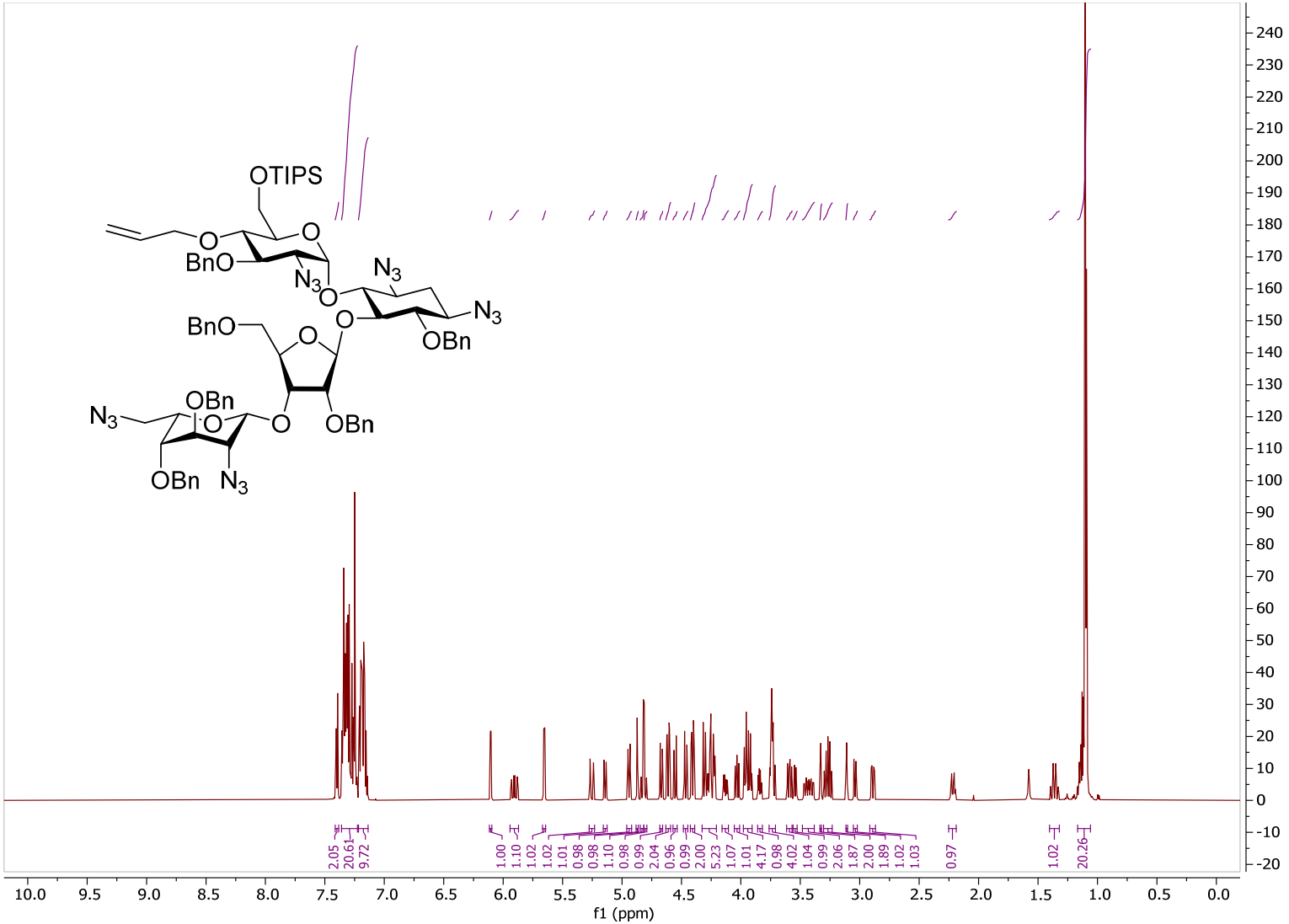
4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (6). HSQC



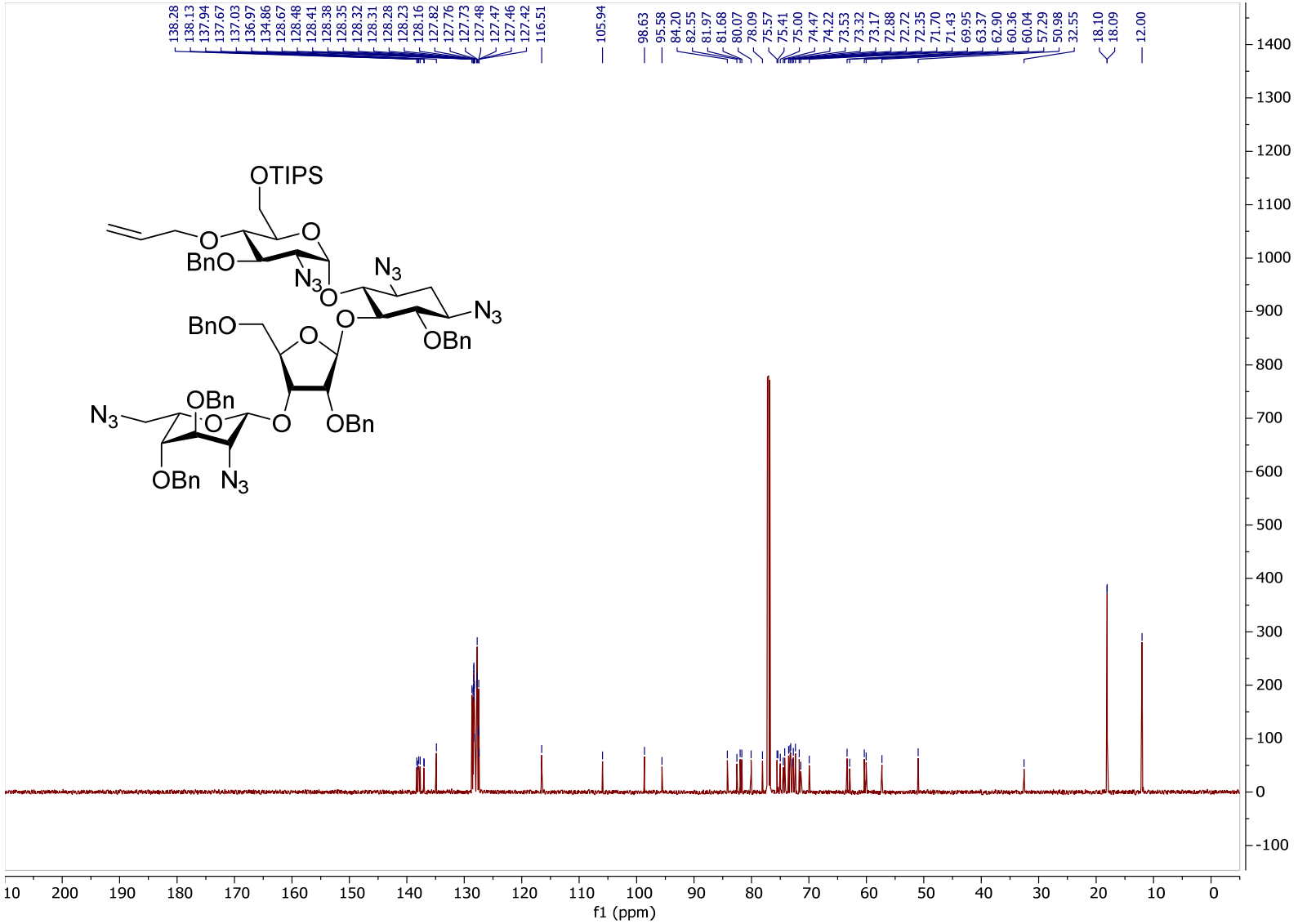
4-*O*-(2-Amino-4,7-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-heptapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (6). HMBC



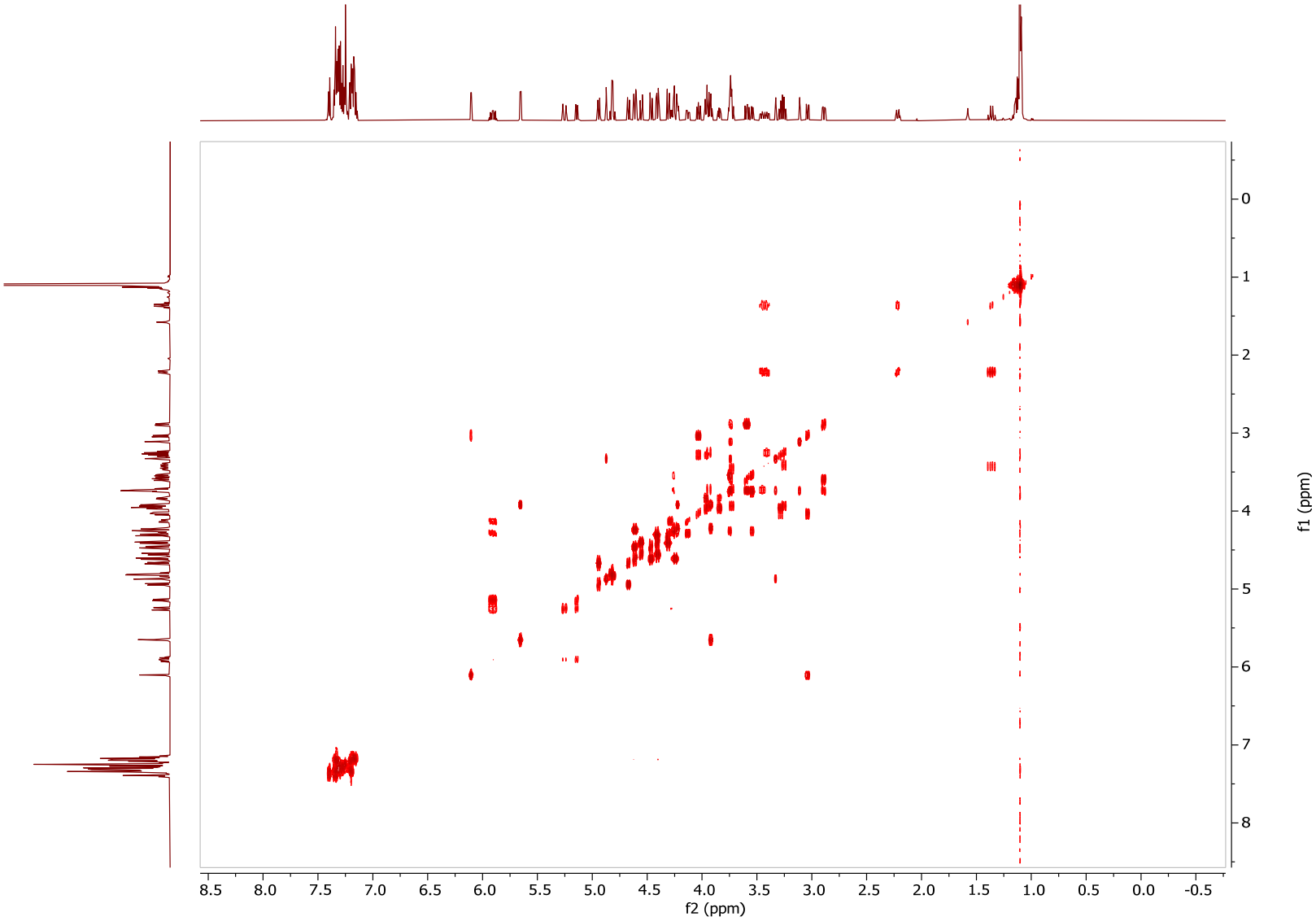
4'-*O*-Allyl-1,3,2',2''',6'''-Pentaazido-6,3',2'',5'',3''',4'''-hexa-*O*-benzyl-6'-*O*-triisopropylsilyl-1,3,2',2''',6'''-pentadeaminoparomomycin (17) ^{1}H NMR (600 MHz, $CDCl_3$)



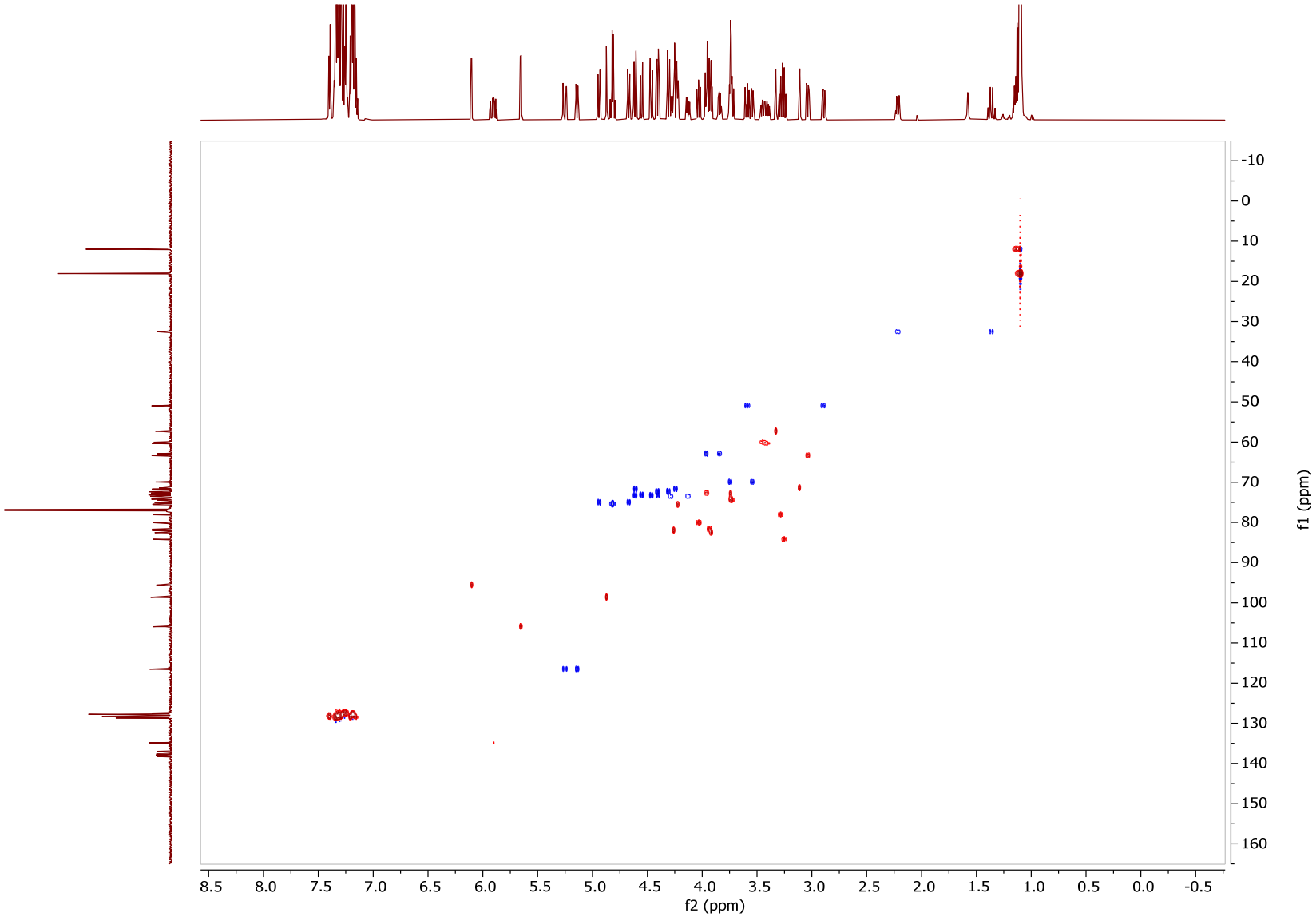
4'-*O*-Allyl-1,3,2',2''',6'''-Pentaazido-6,3',2'',5'',3''',4'''-hexa-*O*-benzyl-6'-*O*-triisopropylsilyl-1,3,2',2''',6'''-pentadeaminoparomomycin (17). ^{13}C NMR (151 MHz, $CDCl_3$)



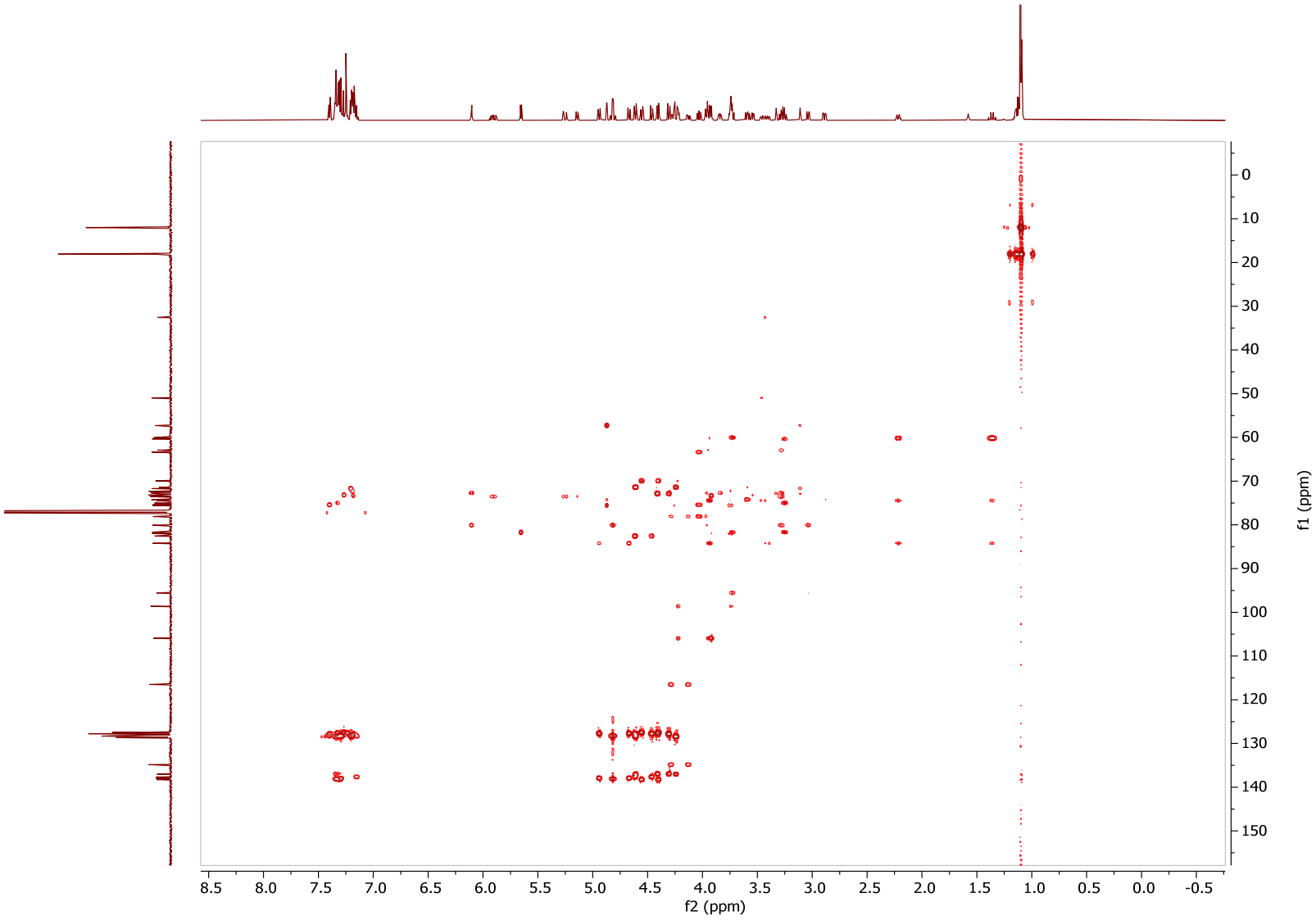
4’-*O*-Allyl-1,3,2’,2’’’,6’’’-Pentaazido-6,3’,2’’,5’’,3’’’,4’’’-hexa-*O*-benzyl-6’-*O*-triisopropylsilyl-1,3,2’,2’’’,6’’’-pentadeaminoparomomycin (17)
COSY



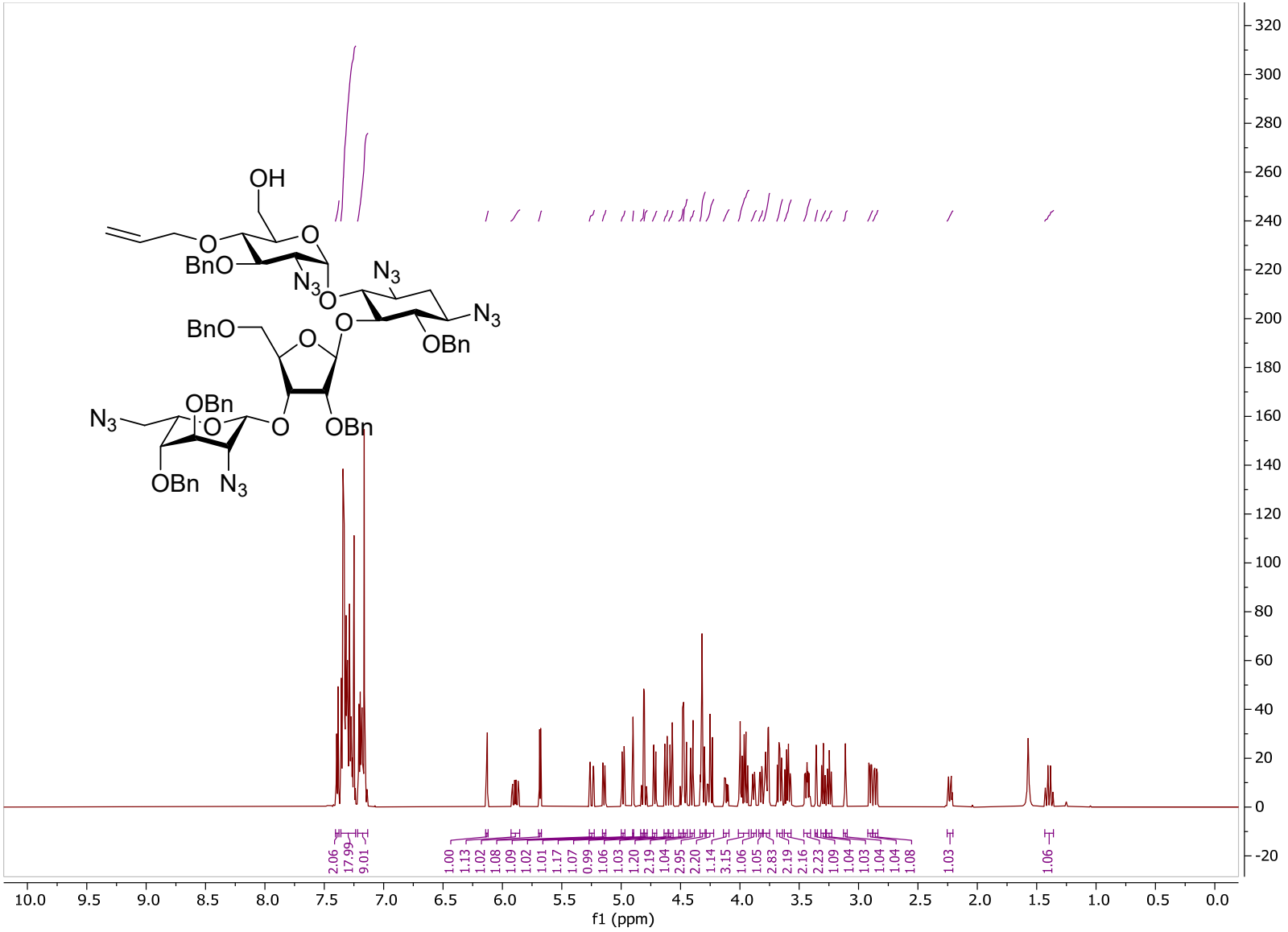
4'-*O*-Allyl-1,3,2',2''',6'''-Pentaazido-6,3',2'',5'',3''',4'''-hexa-*O*-benzyl-6'-*O*-triisopropylsilyl-1,3,2',2''',6'''-pentadeaminoparomomycin (17)
HSQC



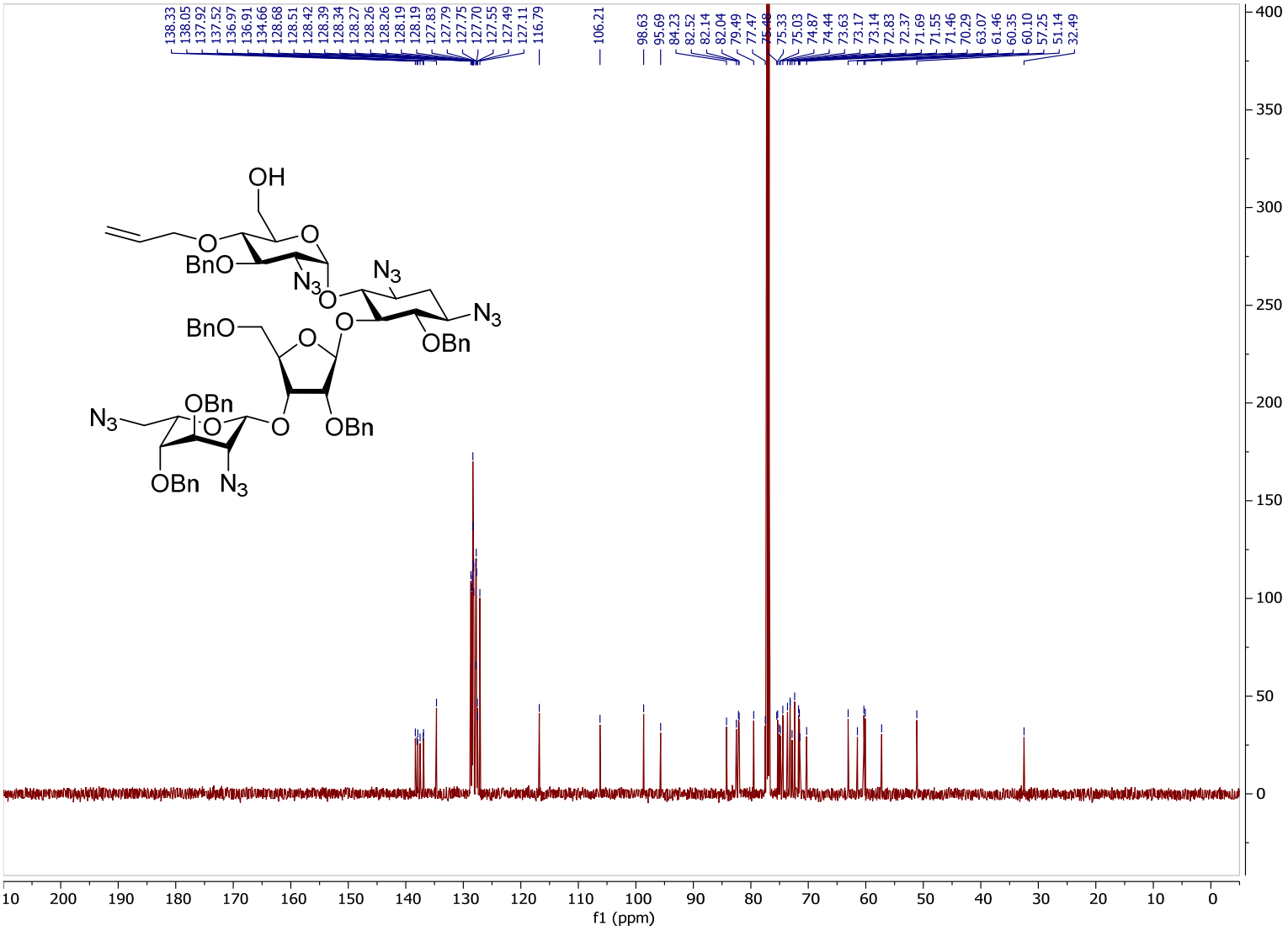
4’-*O*-Allyl-1,3,2’,2’’’,6’’’-Pentaazido-6,3’,2’’,5’’,3’’’,4’’’-hexa-*O*-benzyl-6’-*O*-triisopropylsilyl-1,3,2’,2’’’,6’’’-pentadeaminoparomomycin (17)
HMBC



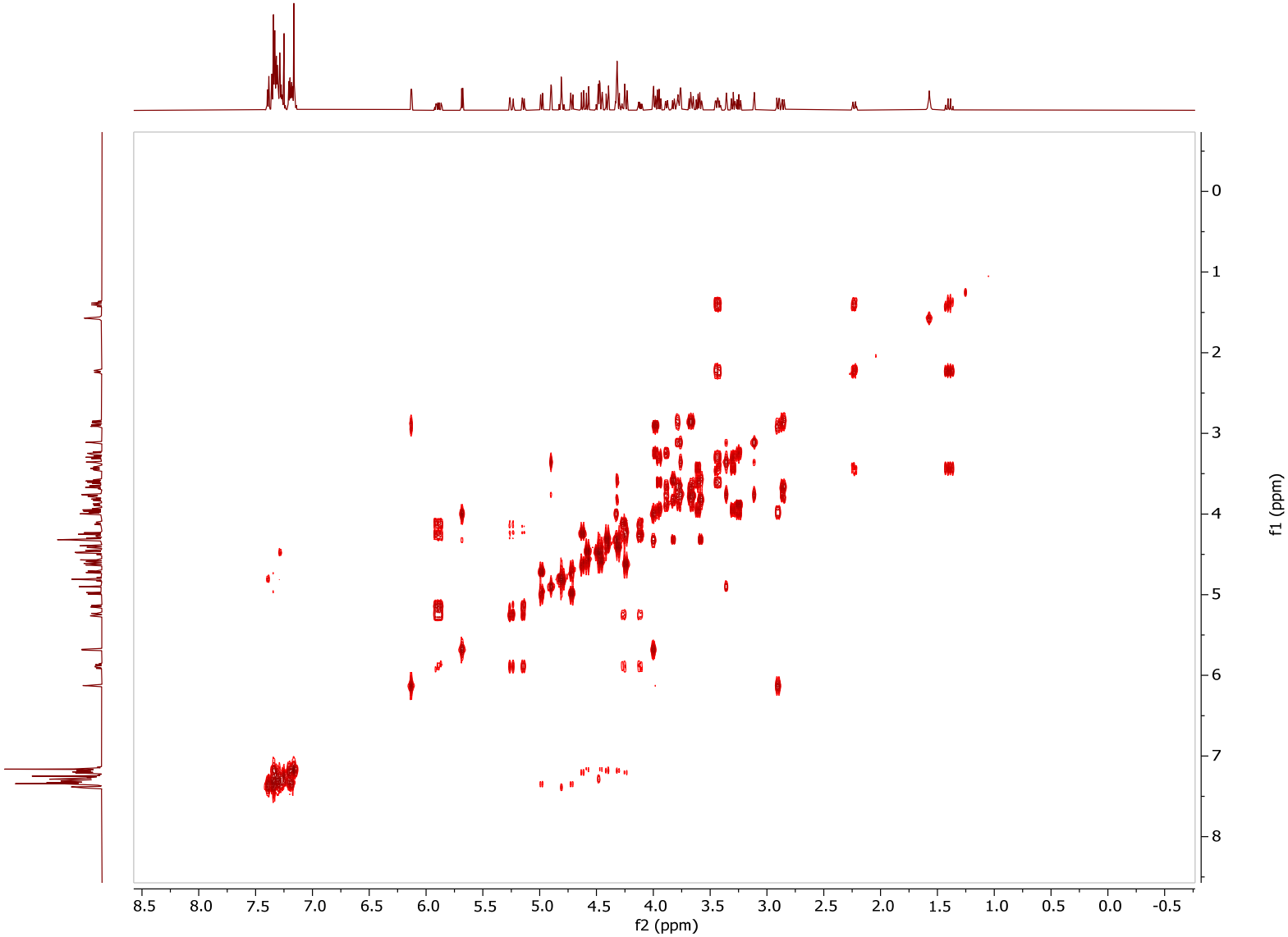
4'-*O*-Allyl-1,3,2',2''',6'''-Pentaazido-6,3',2'',5'',3''',4'''-hexa-*O*-benzyl-1,3,2',2''',6'''-pentadeaminoparomomycin (18) ^{1}H NMR (600 MHz, $CDCl_3$)



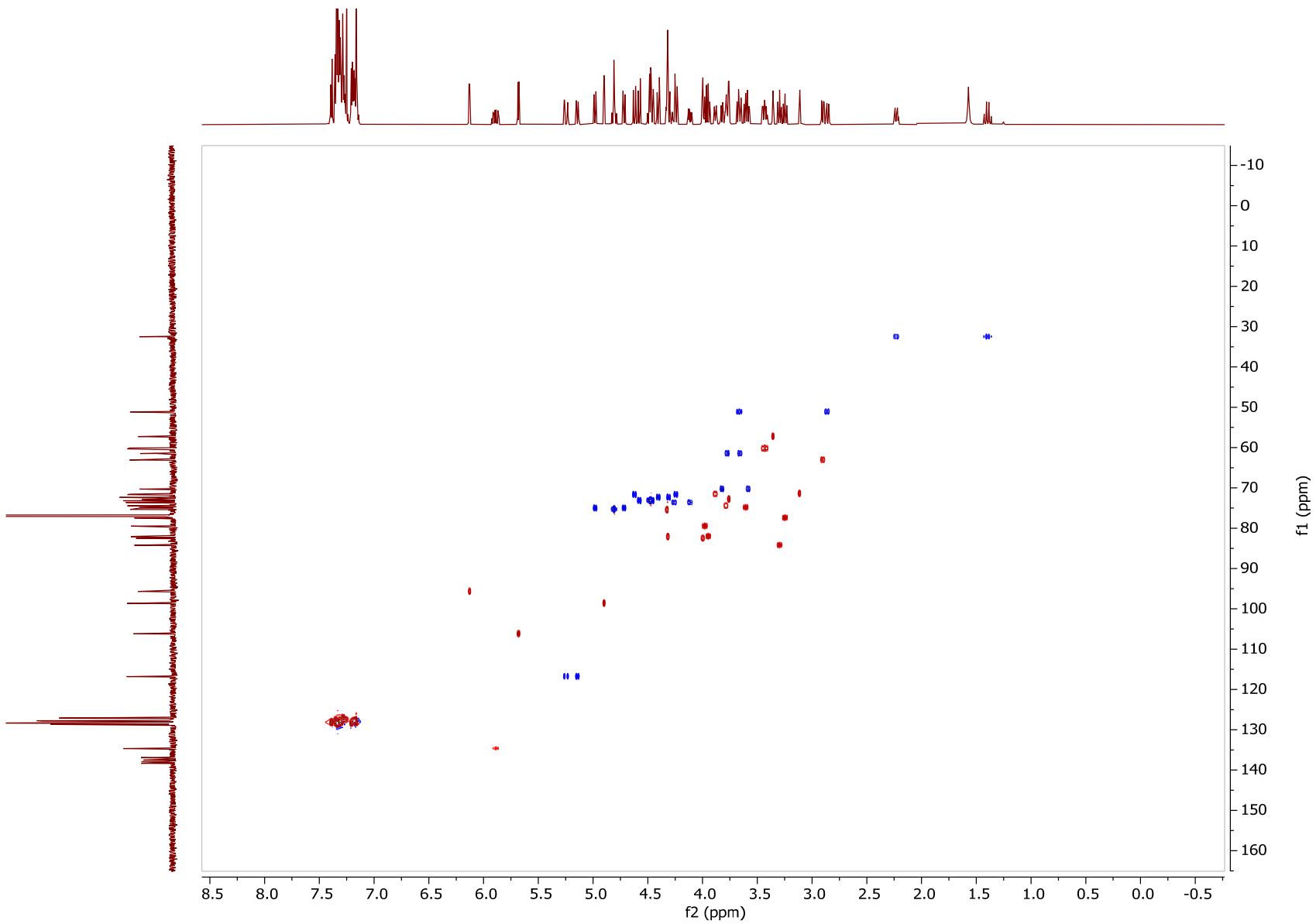
4'-*O*-Allyl-1,3,2',2''',6'''-Pentaazido-6,3',2'',5'',3''',4'''-hexa-*O*-benzyl-1,3,2',2''',6'''-pentadeaminoparomomycin (18) ^{13}C NMR (151 MHz, $CDCl_3$)



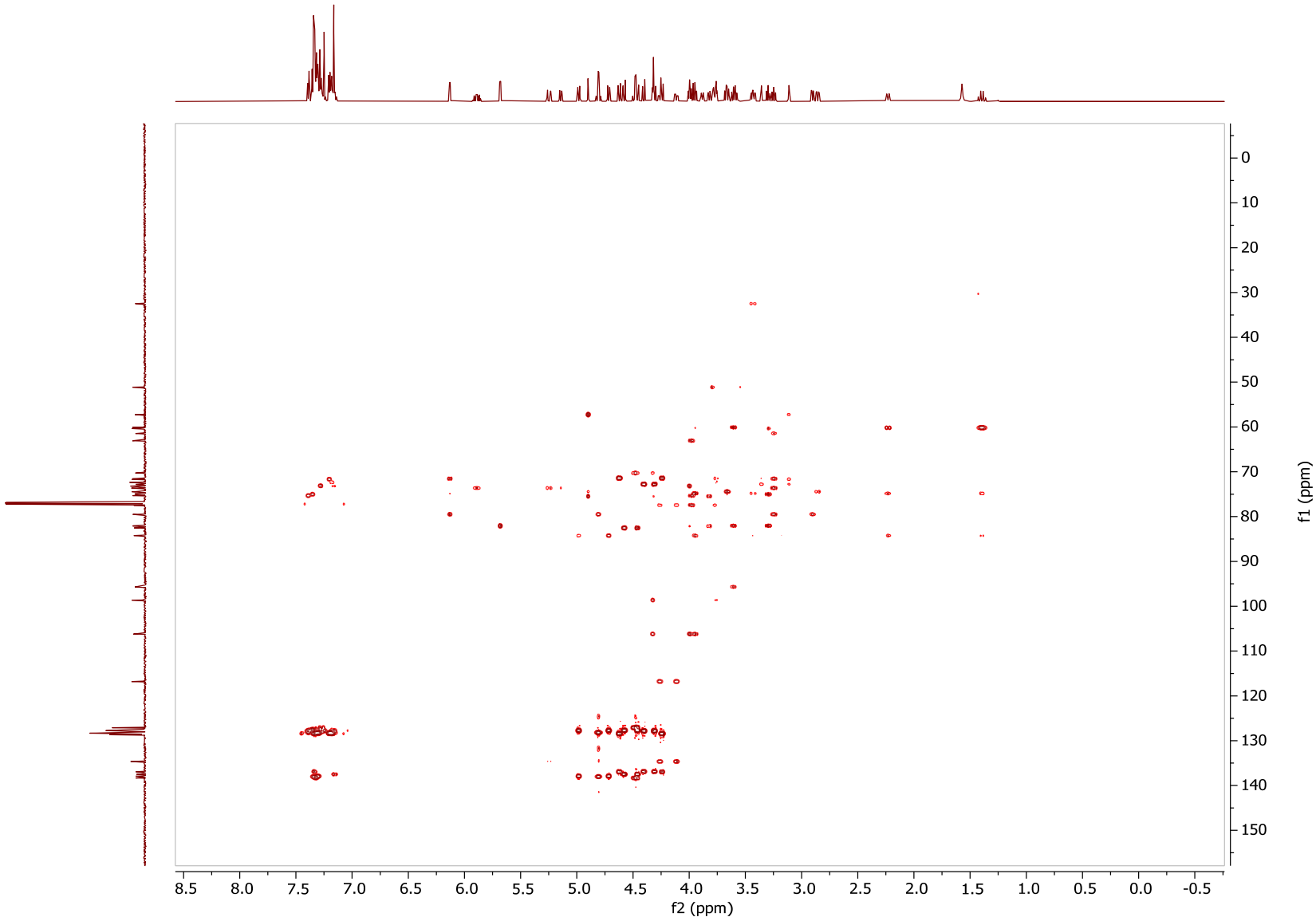
4'-*O*-Allyl-1,3,2',2''',6'''-Pentaazido-6,3',2'',5'',3''',4'''-hexa-*O*-benzyl-1,3,2',2''',6'''-pentadeaminoparomomycin (18) COSY



4'-*O*-Allyl-1,3,2',2''',6'''-Pentaazido-6,3',2'',5'',3''',4'''-hexa-*O*-benzyl-1,3,2',2''',6'''-pentadeaminoparomomycin (18) HSQC



4'-*O*-Allyl-1,3,2',2''',6'''-Pentaazido-6,3',2'',5'',3''',4'''-hexa-*O*-benzyl-1,3,2',2''',6'''-pentadeaminoparomomycin (18) HMBC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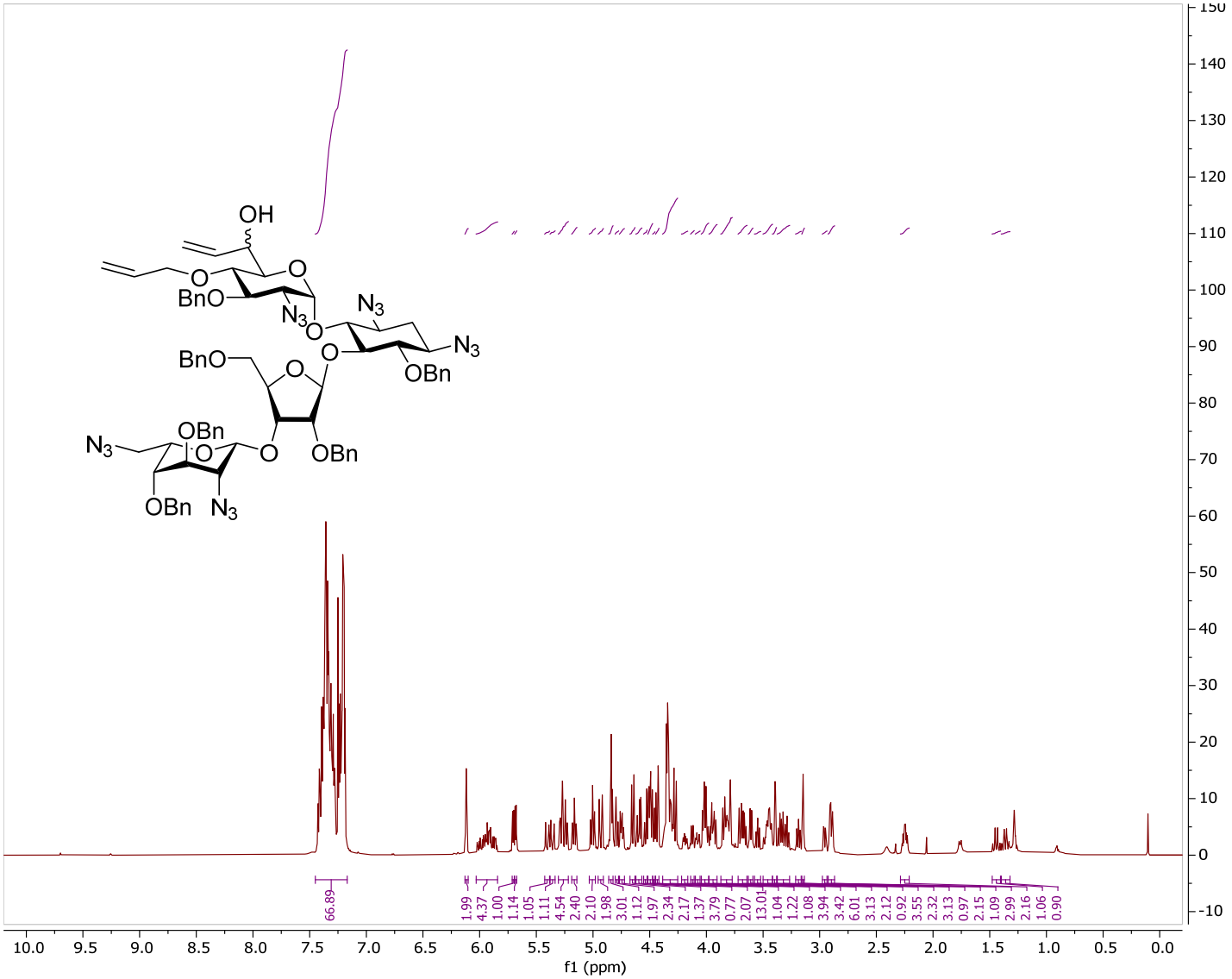
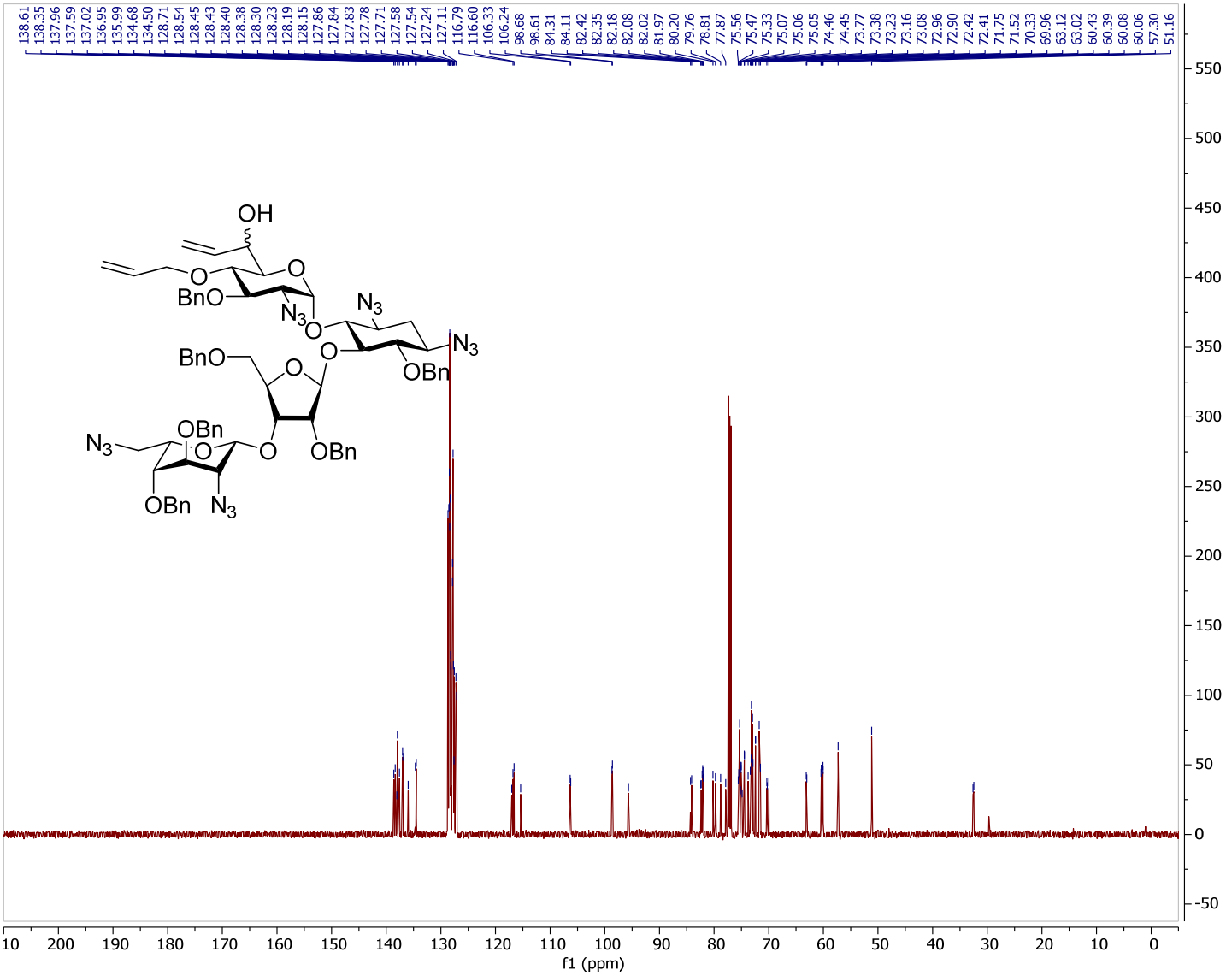
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

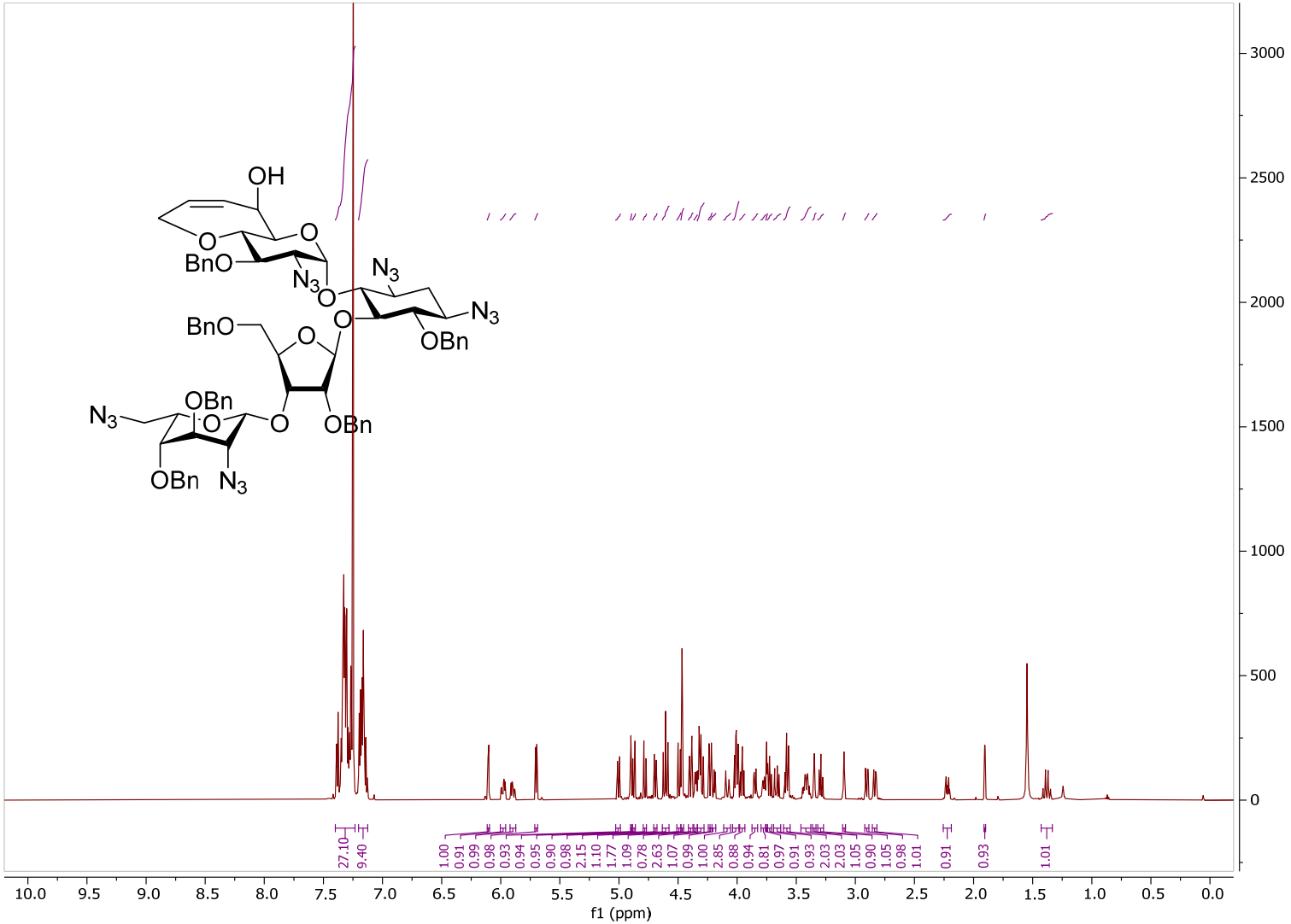
4'-*O*-Allyl-1,3,2',2''',6'''-Pentaazido-6,3',2'',5'',3''',4'''-hexa-*O*-benzyl-6'-*C*-vinyl-1,3,2',2''',6'''-pentadeaminoparomomycin (19) ^{1}H NMR (600 MHz, $CDCl_3$)



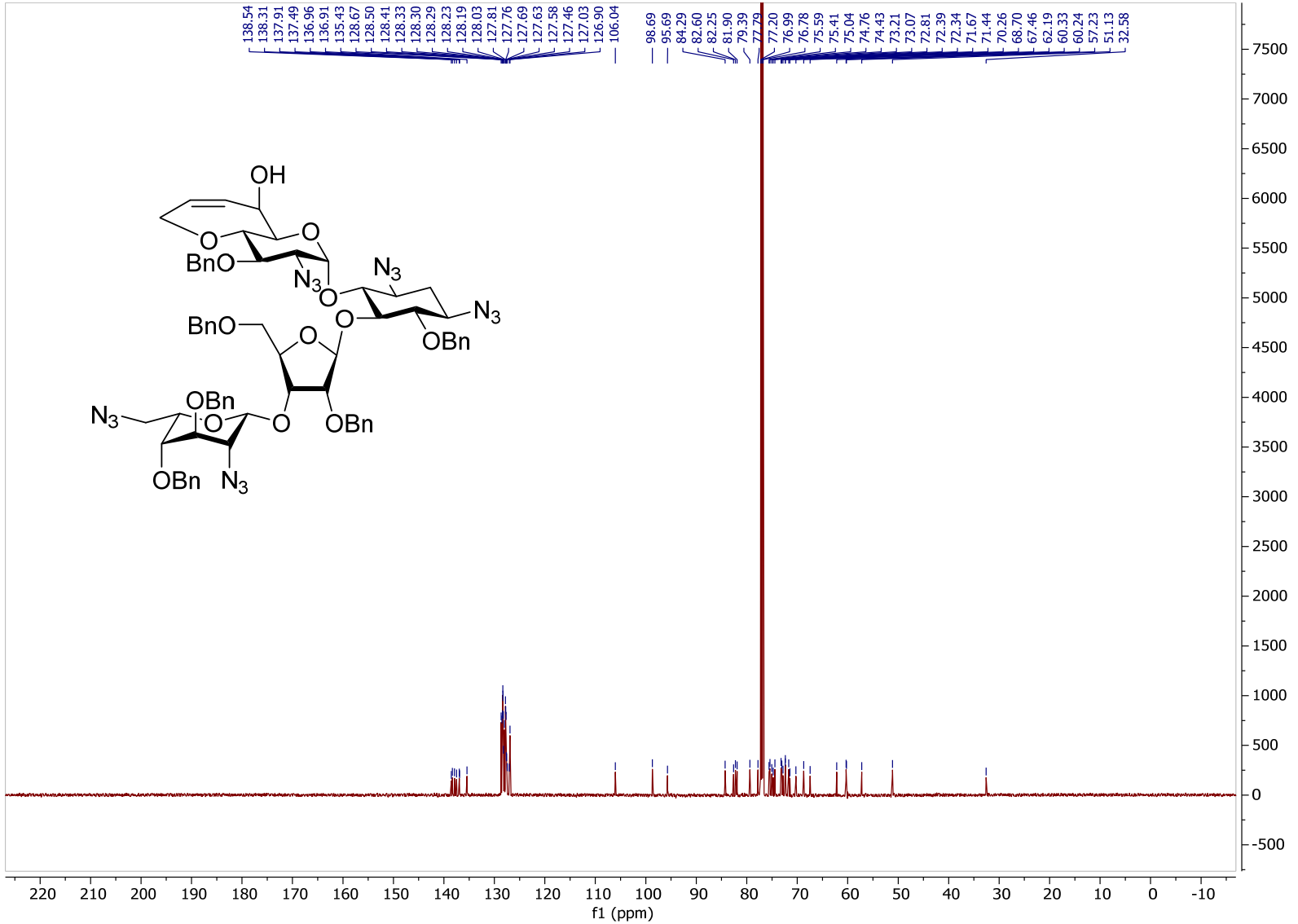
4'-*O*-Allyl-1,3,2',2''',6'''-Pentaazido-6,3',2'',5'',3''',4'''-hexa-*O*-benzyl-6'-*C*-vinyl-1,3,2',2''',6'''-pentadeaminoparomomycin (19) ^{13}C NMR (151 MHz, $CDCl_3$)



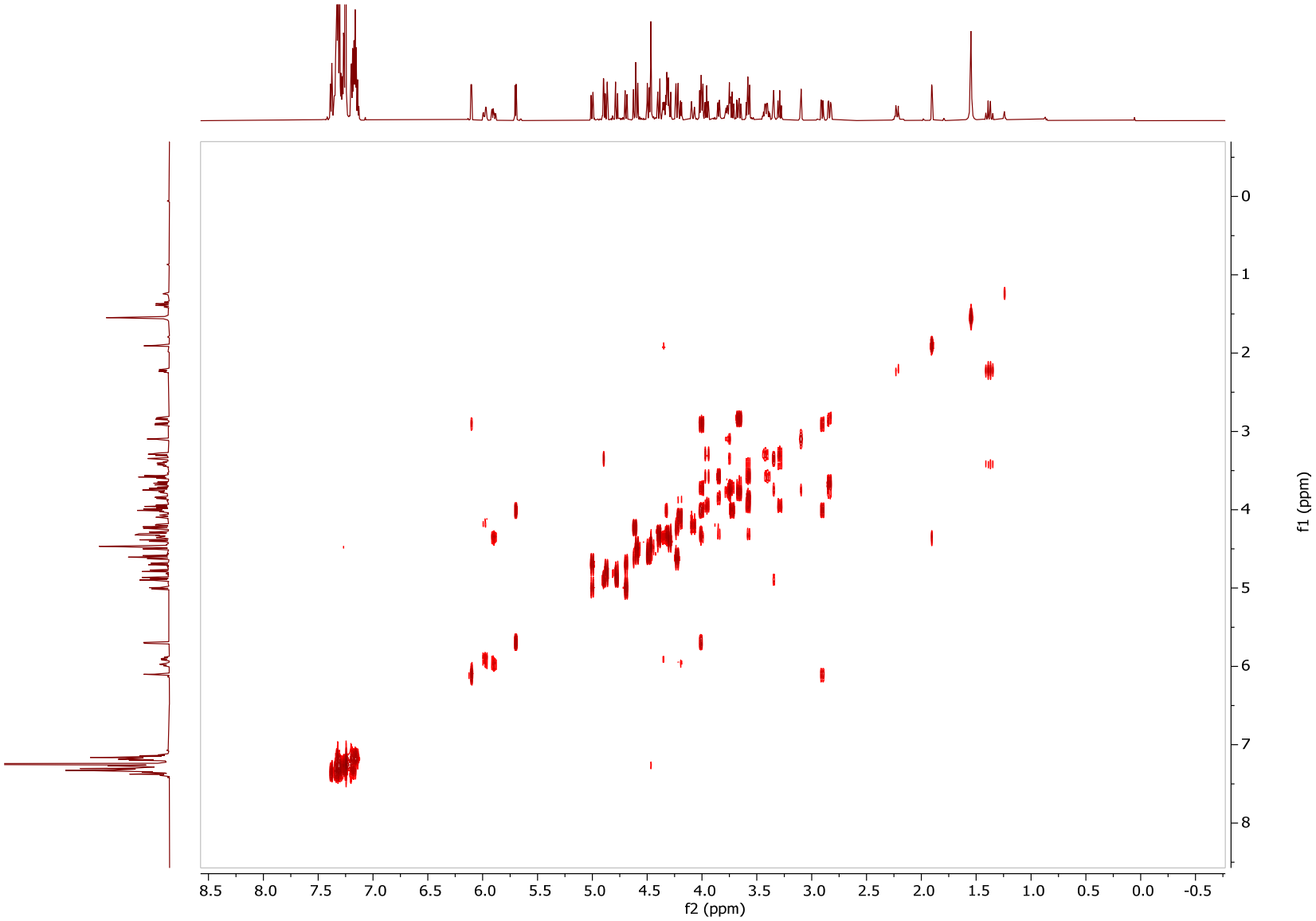
4-*O*-(2-Azido-3-*O*-benzyl-4,8-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-nona-7-enopyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (20(ax)) ^{1}H NMR (600 MHz, $CDCl_3$)



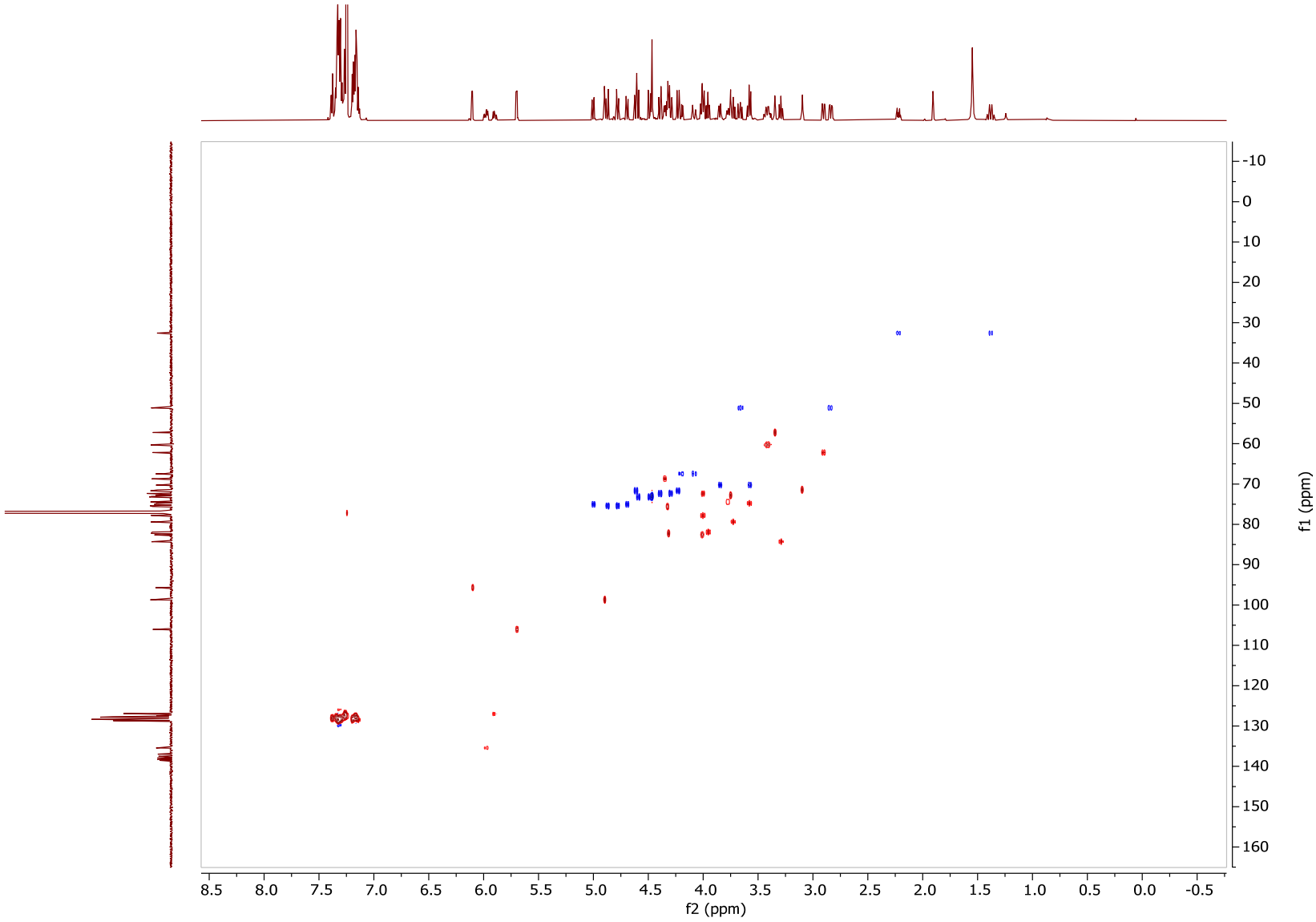
4-*O*-(2-Azido-3-*O*-benzyl-4,8-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-nona-7-enopyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (20(ax)) ^{13}C NMR (151 MHz, $CDCl_3$)



4-*O*-(2-Azido-3-*O*-benzyl-4,8-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-nona-7-enopyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (20(ax)) COSY



4-*O*-(2-Azido-3-*O*-benzyl-4,8-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-nona-7-enopyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (20(ax)) HSQC



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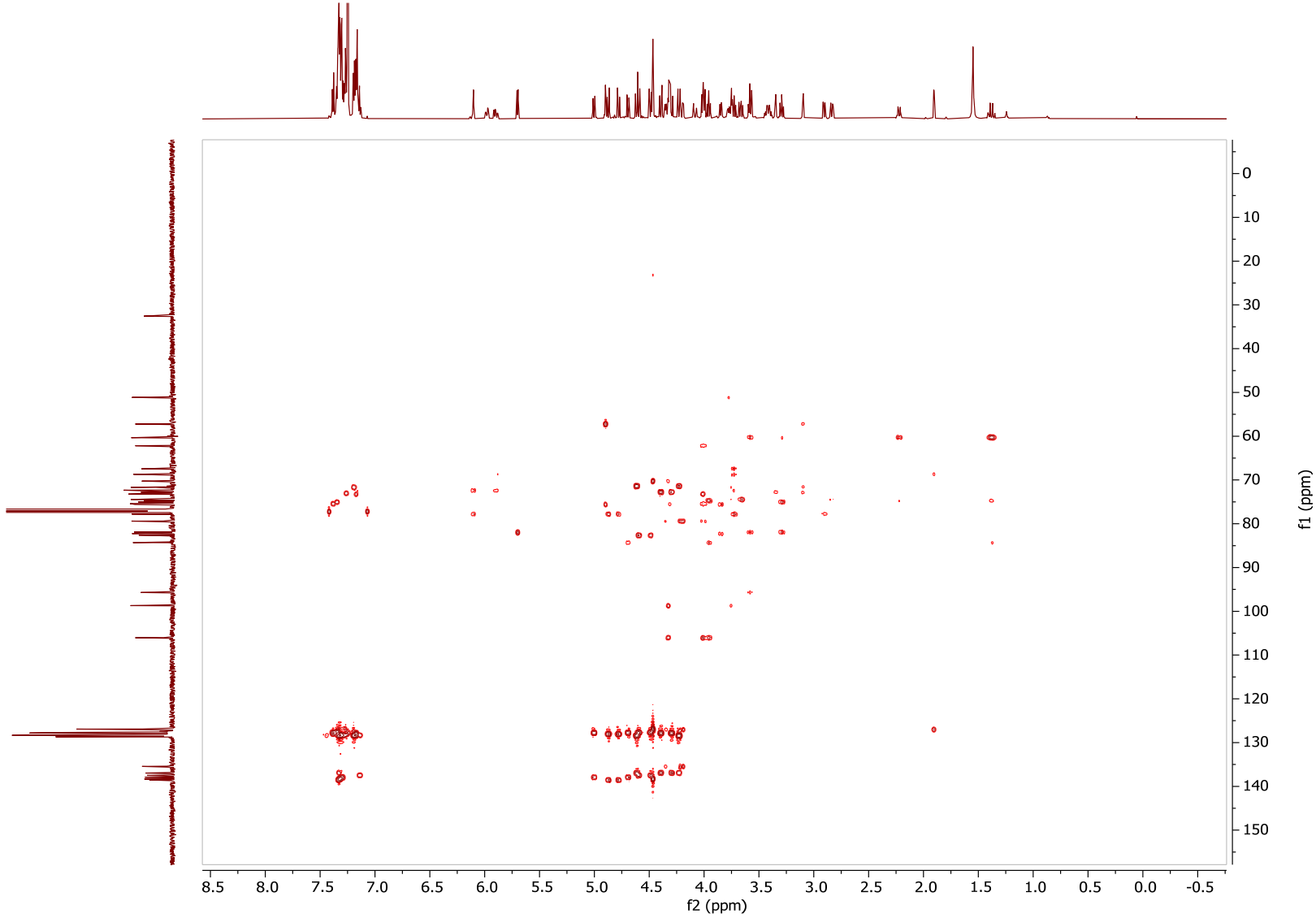
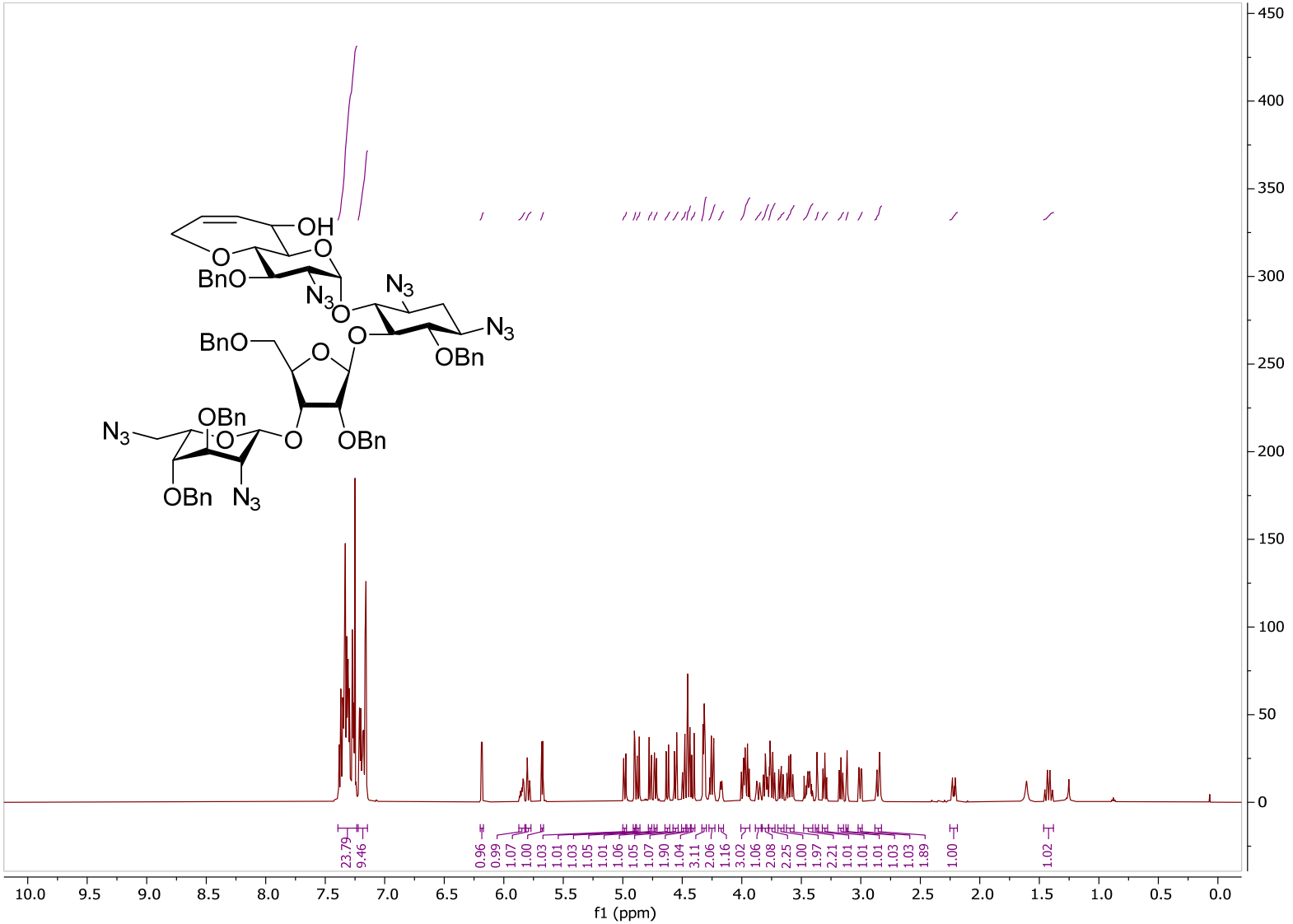
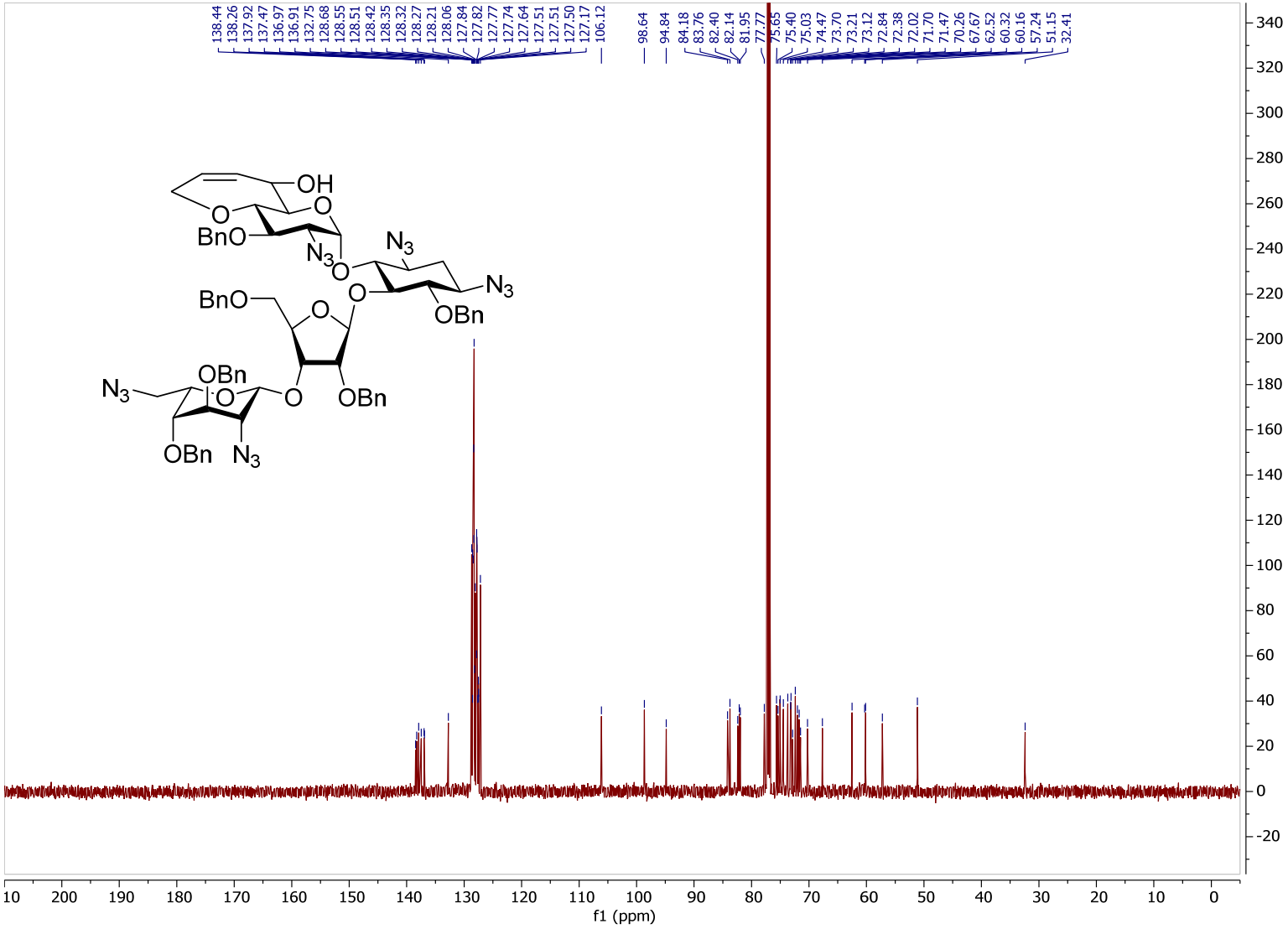


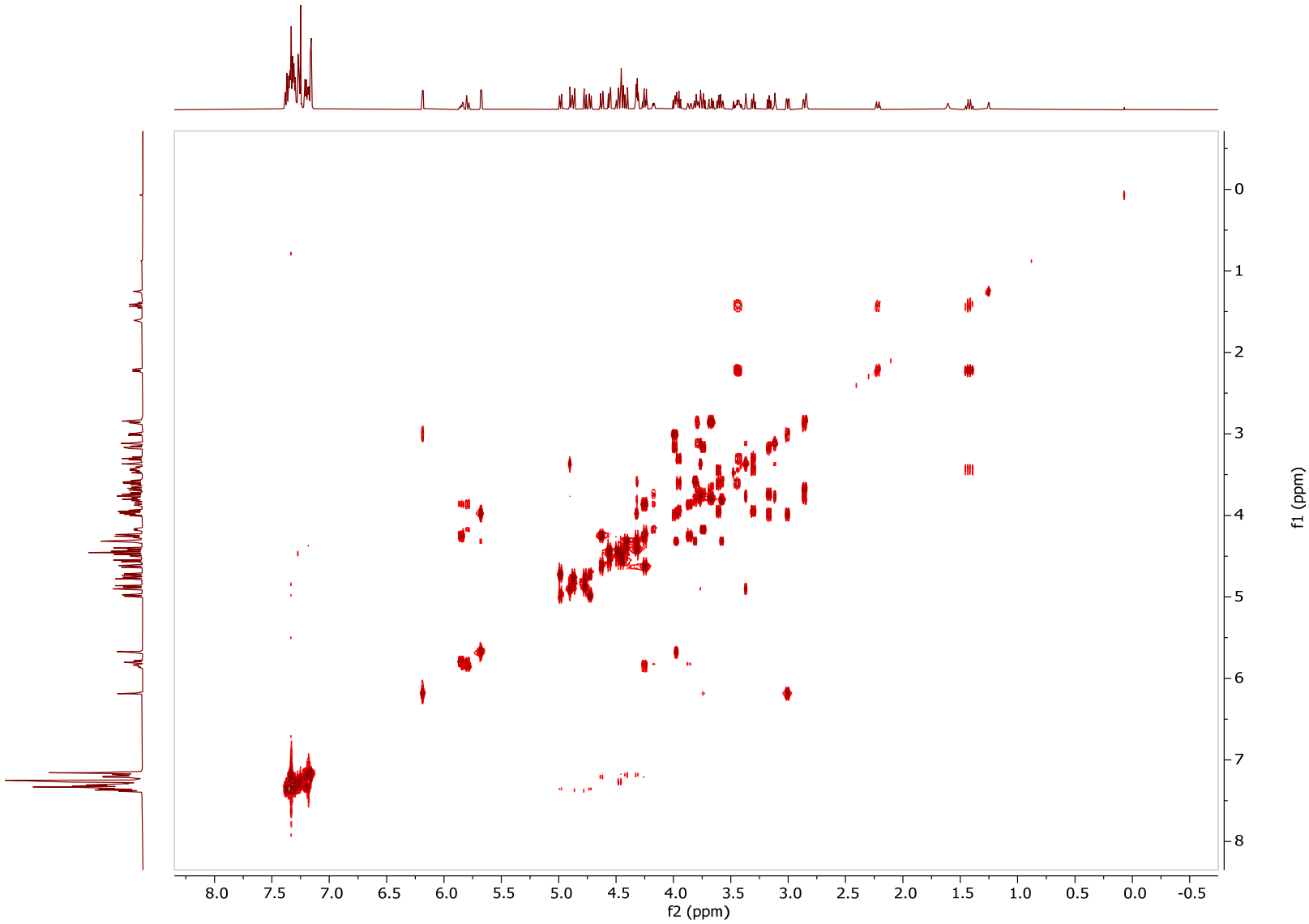
4-*O*-(2-Azido-3-*O*-benzyl-4,8-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-nona-7-enopyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (20(eq)) ^{1}H NMR (600 MHz, $CDCl_3$)



4-*O*-(2-Azido-3-*O*-benzyl-4,8-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-nona-7-enopyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (20(eq)) ^{13}C NMR (151 MHz, $CDCl_3$)



4-*O*-(2-Azido-3-*O*-benzyl-4,8-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-nona-7-enopyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (20(eq)) COSY



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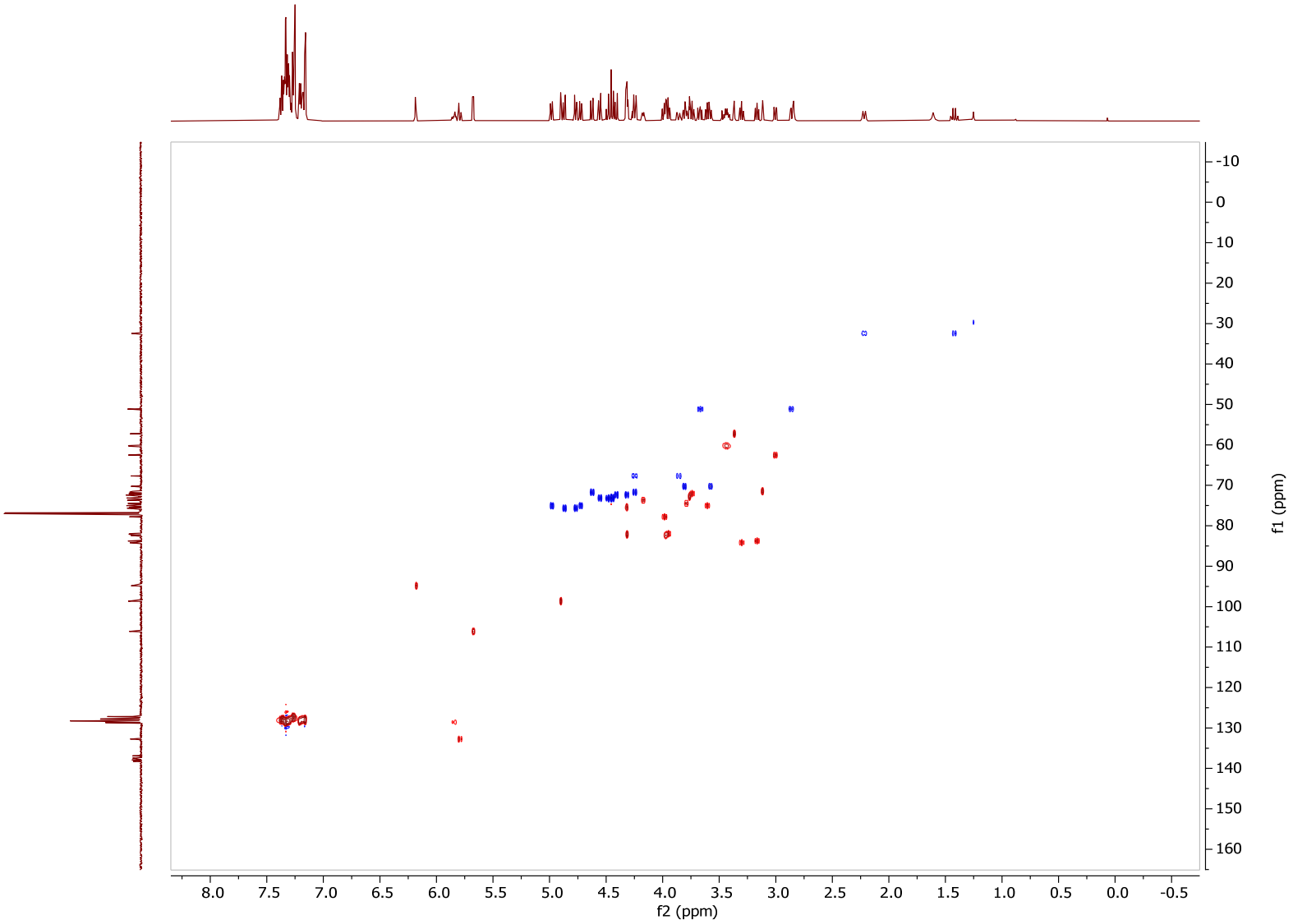
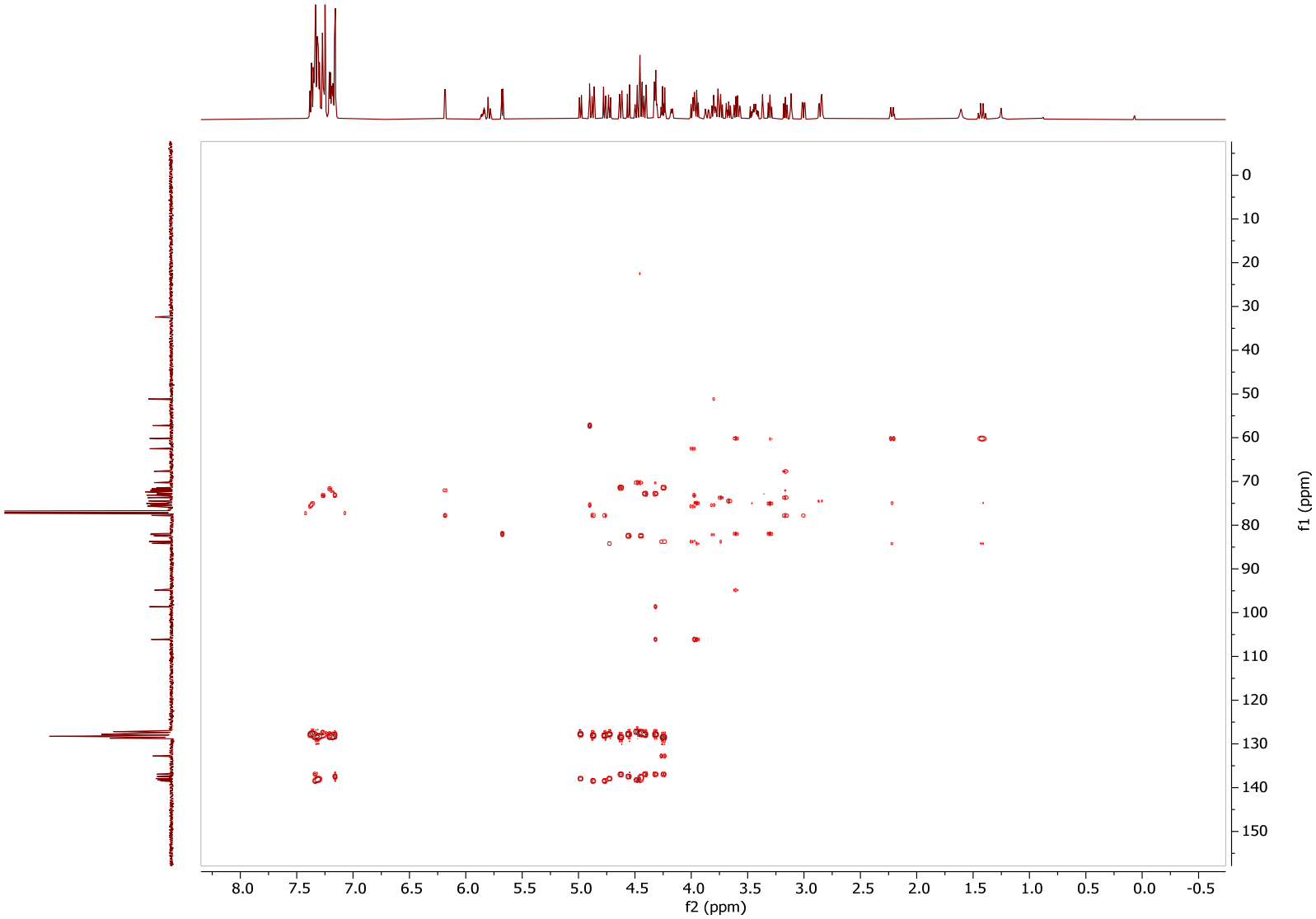
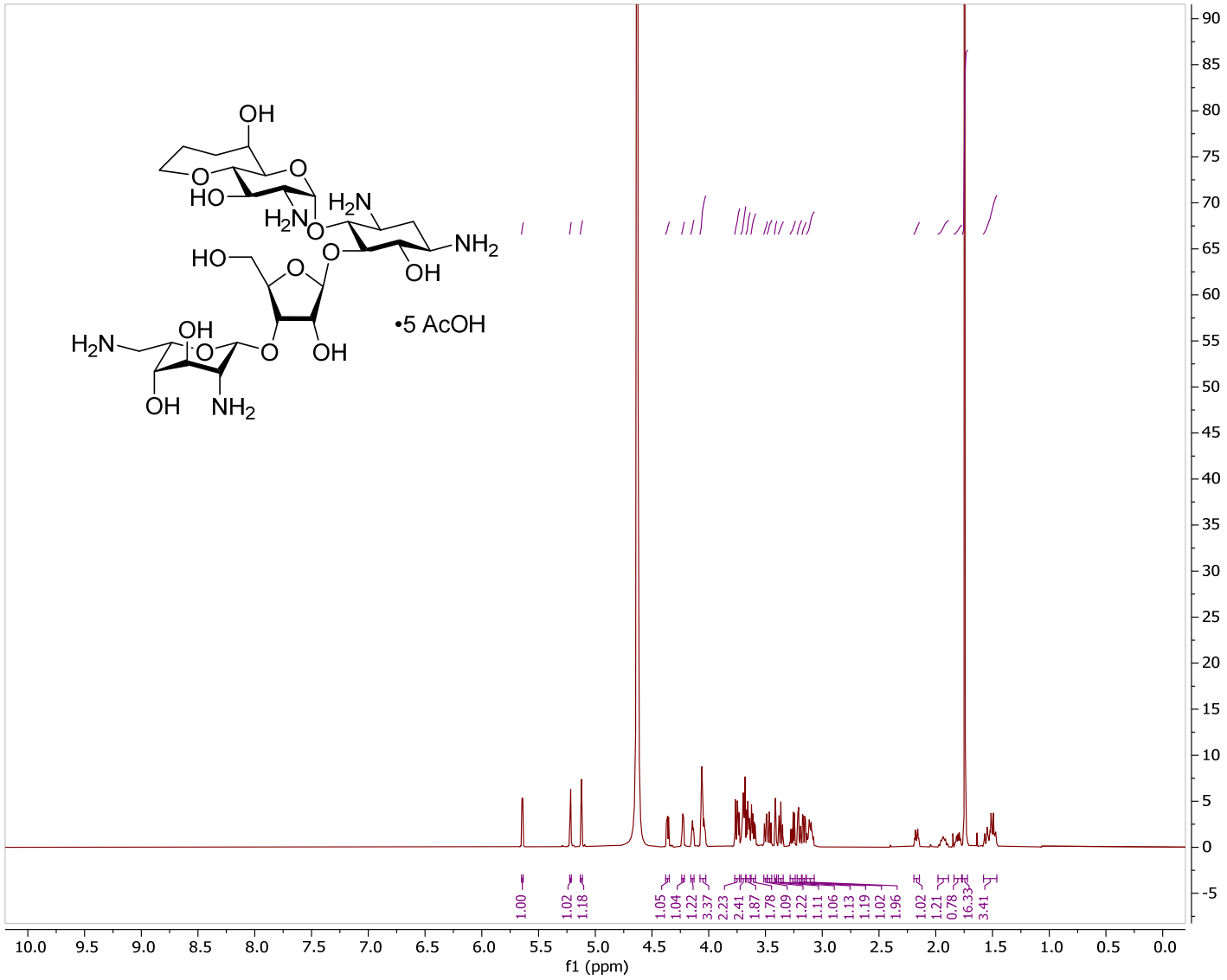


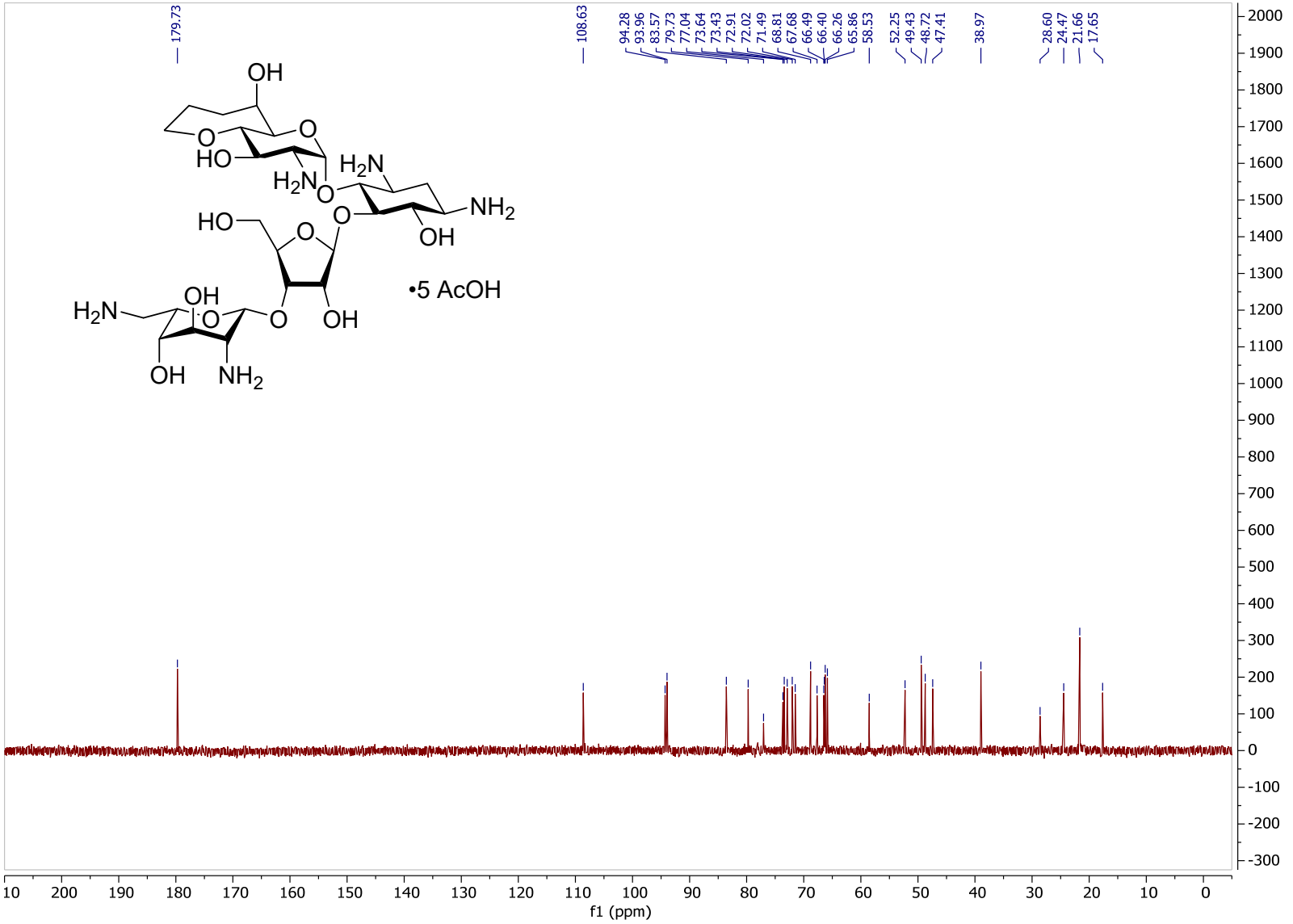
4-*O*-(2-Azido-3-*O*-benzyl-4,8-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-nona-7-enopyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (20(eq)) HMBC



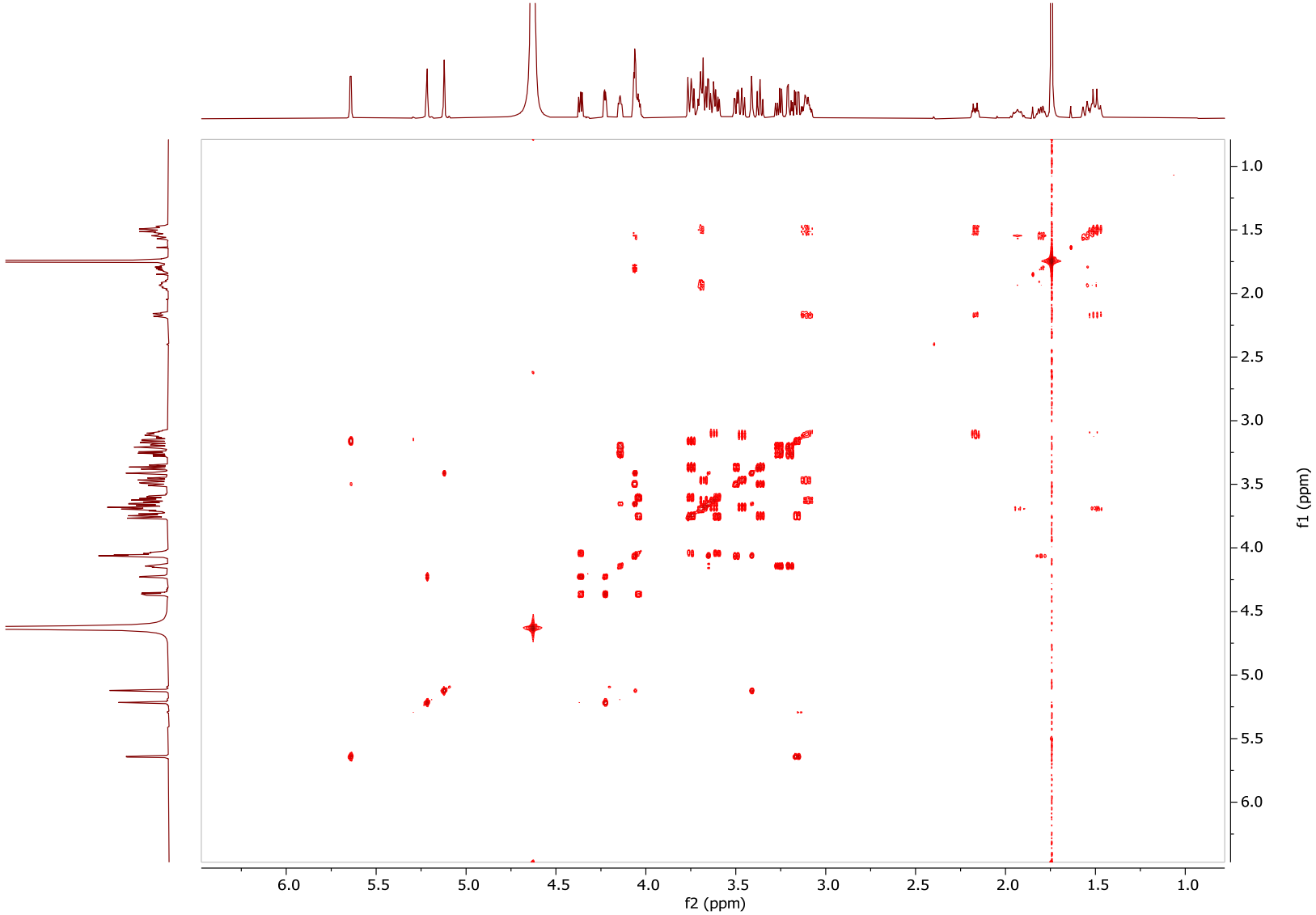
4-*O*-(2-Amino-4,9-anhydro-2,7,8-trideoxy-D-glycero-α-D-gluco-nonapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (9) ^{1}H NMR (600 MHz, D_2O)



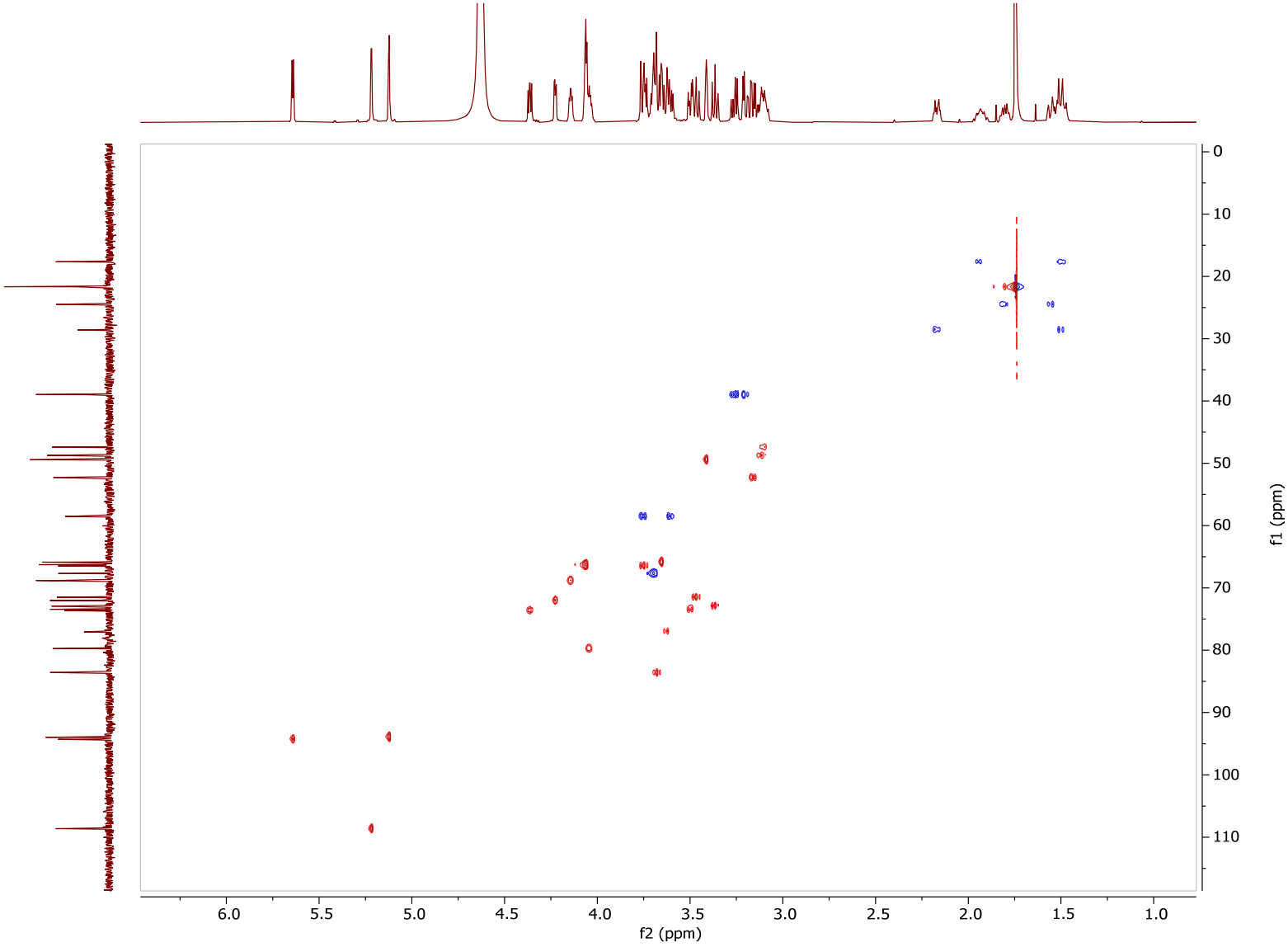
4-*O*-(2-Amino-4,9-anhydro-2,7,8-trideoxy-D-glycero-α-D-gluco-nonapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (9) ^{13}C NMR (151 MHz, D_2O)



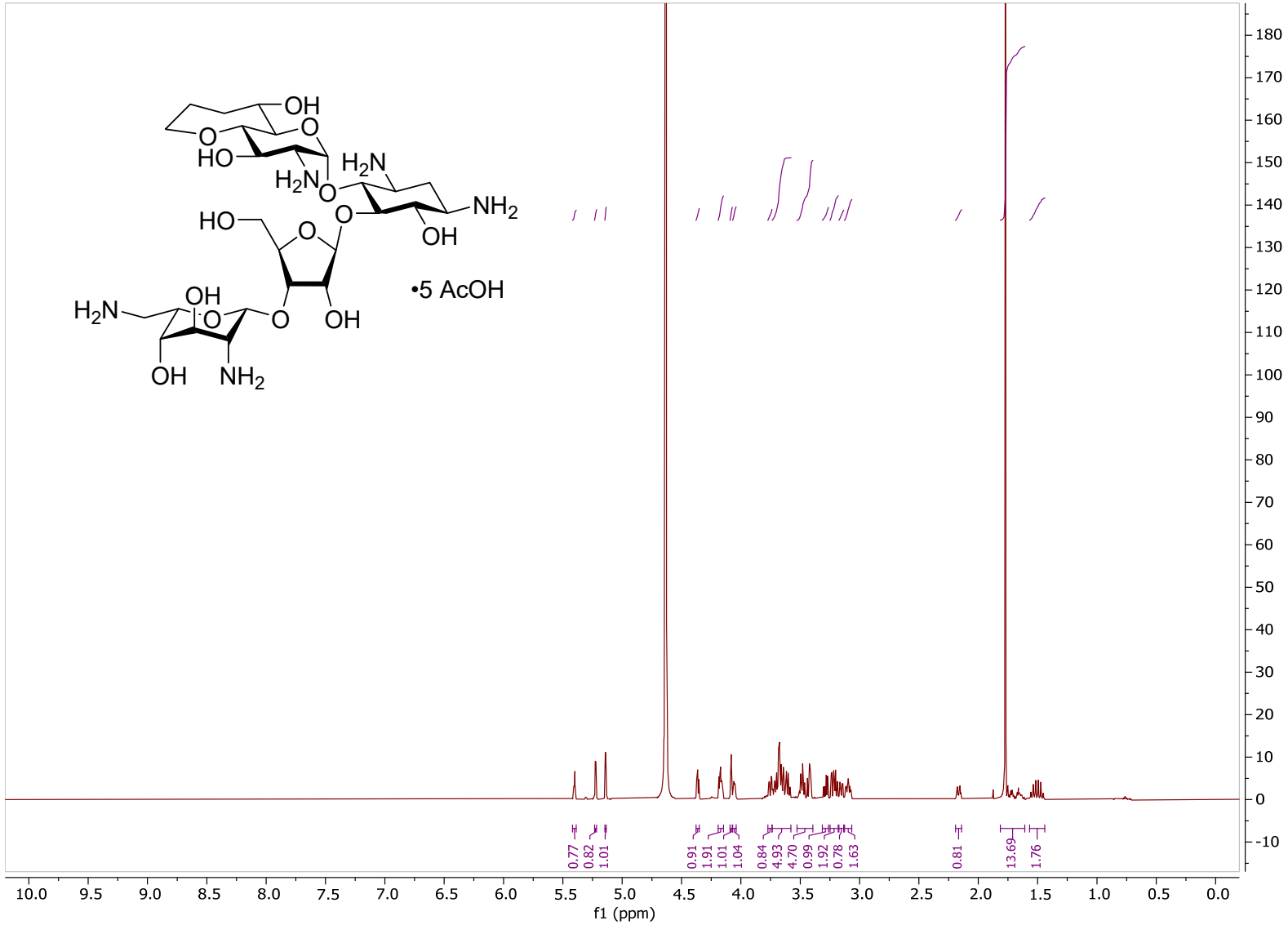
4-*O*-(2-Amino-4,9-anhydro-2,7,8-trideoxy-D-glycero-α-D-gluco-nonapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (9) COSY



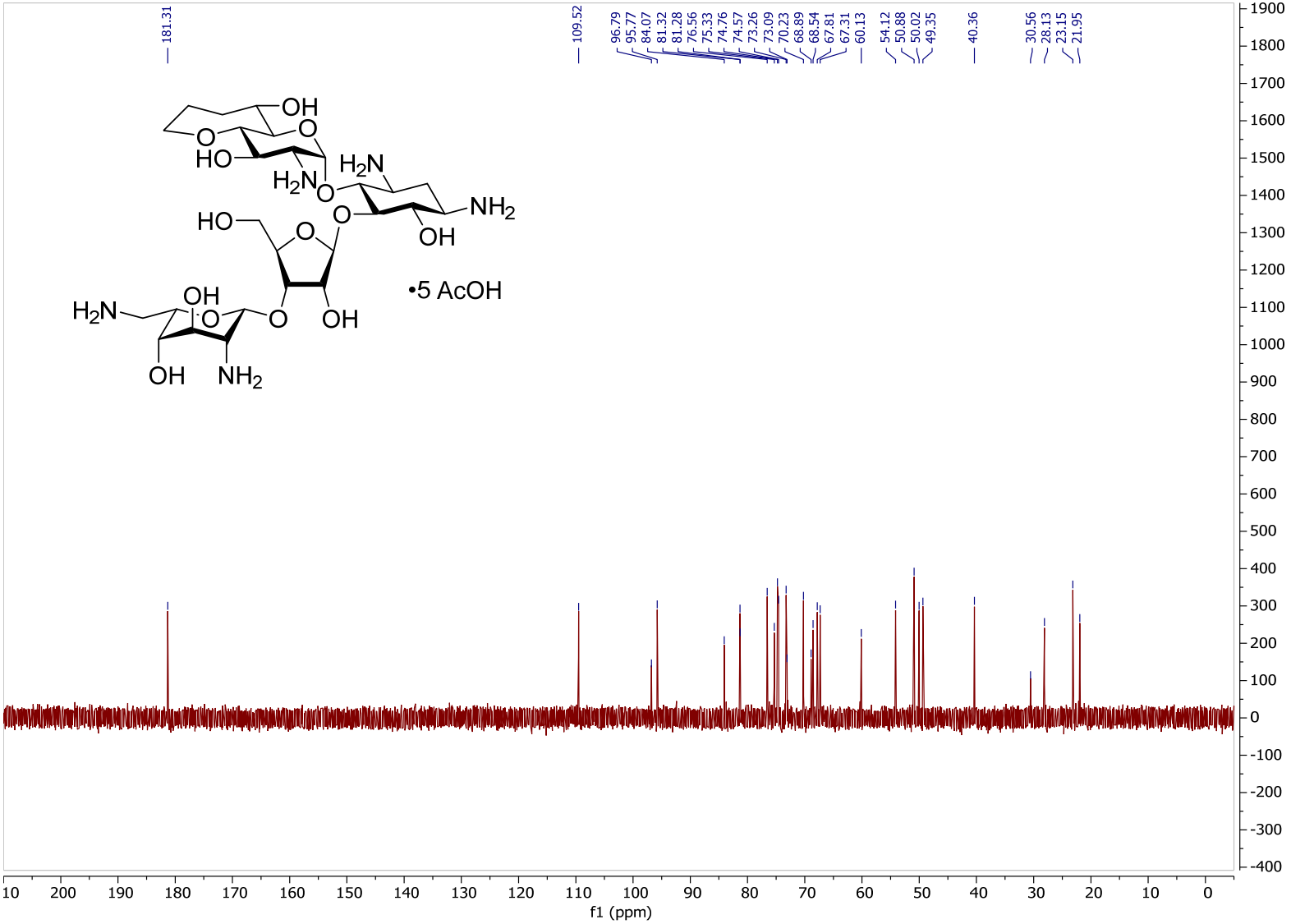
4-*O*-(2-Amino-4,9-anhydro-2,7,8-trideoxy-D-glycero-α-D-gluco-nonapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (9) HSQC



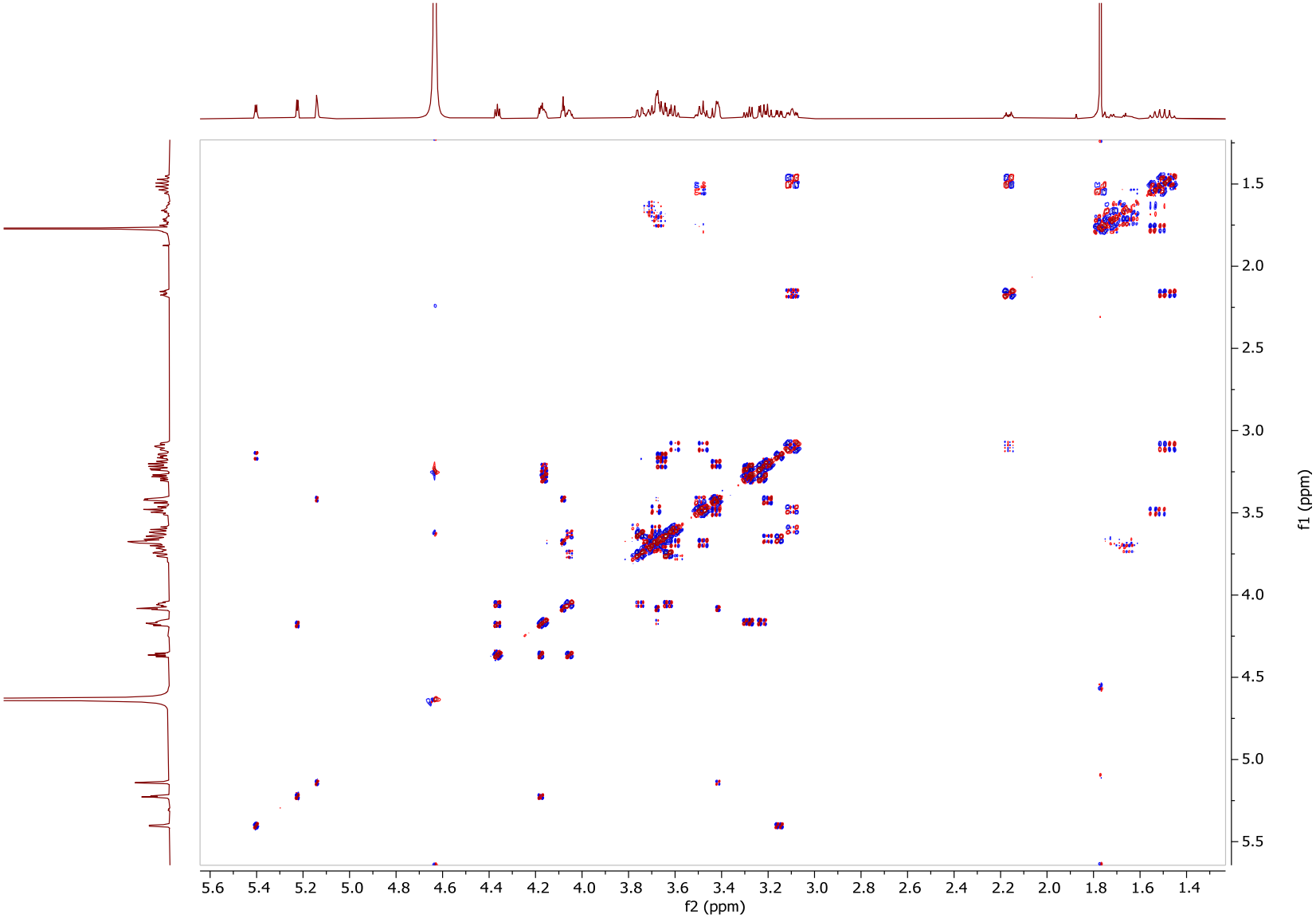
4-*O*-(2-Amino-4,9-anhydro-2,7,8-trideoxy-L-glycero-α-D-gluco-nonapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (8) ^{1}H NMR (600 MHz, D_2O)



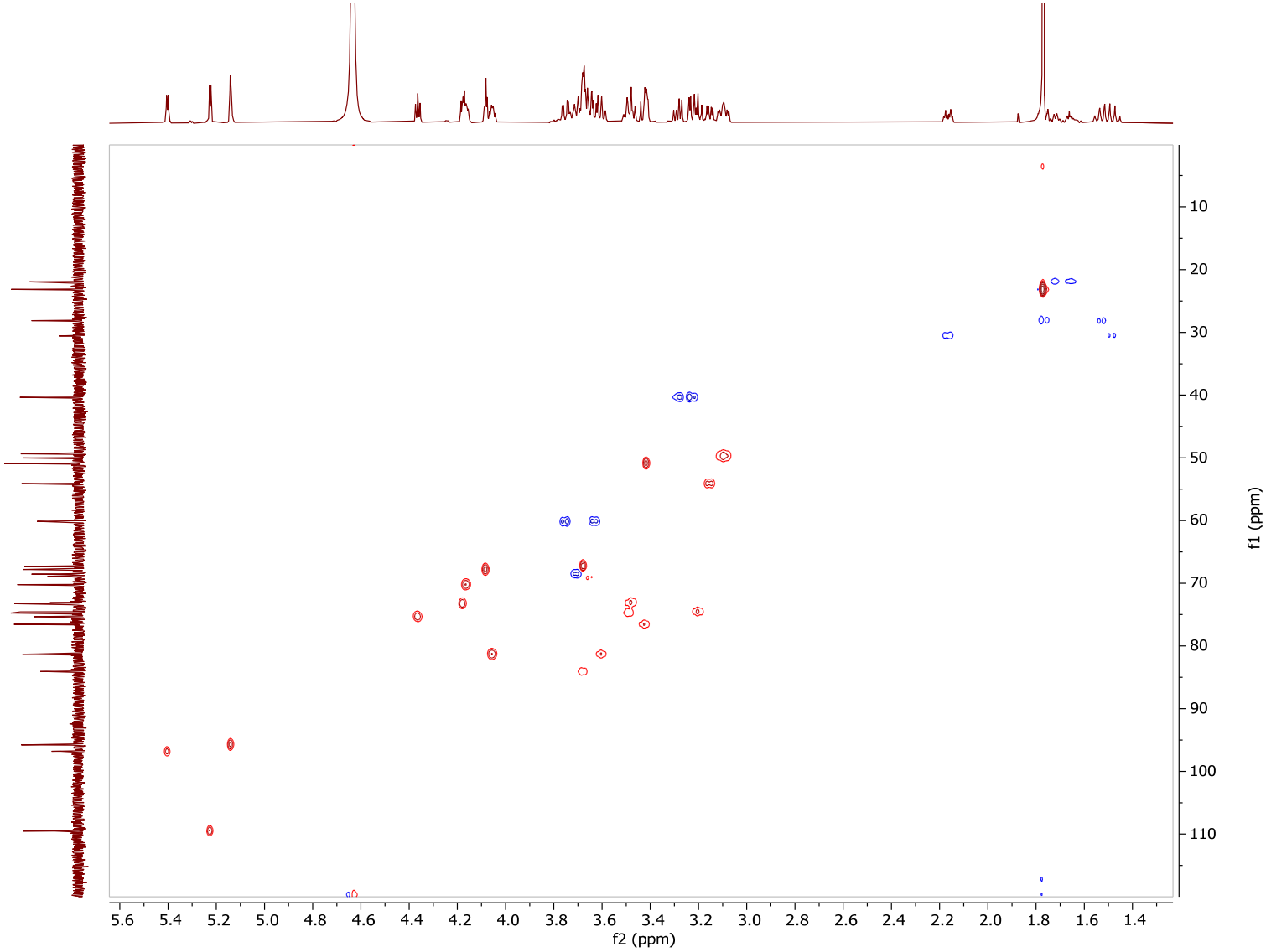
4-*O*-(2-Amino-4,9-anhydro-2,7,8-trideoxy-L-glycero-α-D-gluco-nonapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (8) ^{13}C NMR (151 MHz, D_2O)



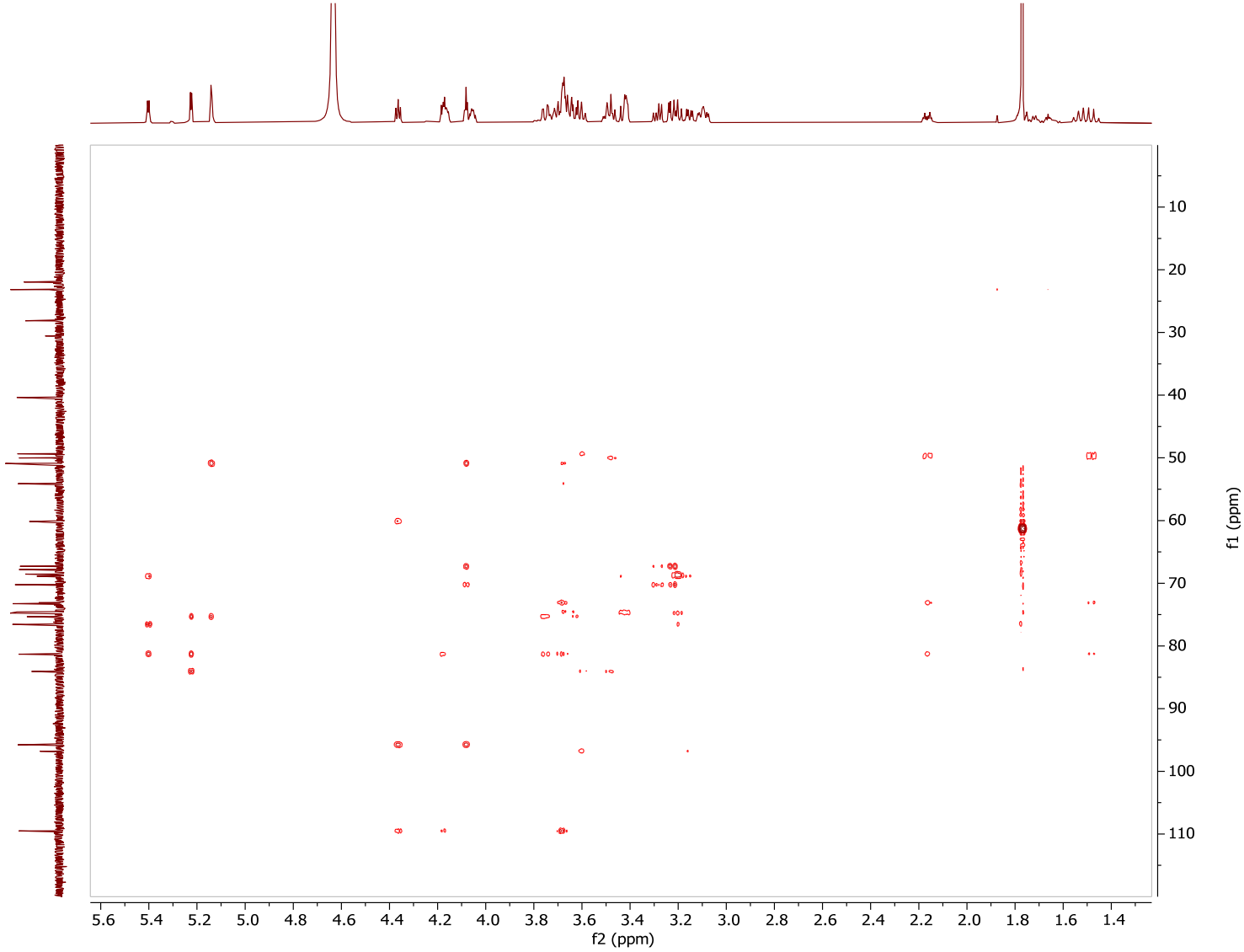
4-*O*-(2-Amino-4,9-anhydro-2,7,8-trideoxy-L-glycero-α-D-gluco-nonapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (8) COSY



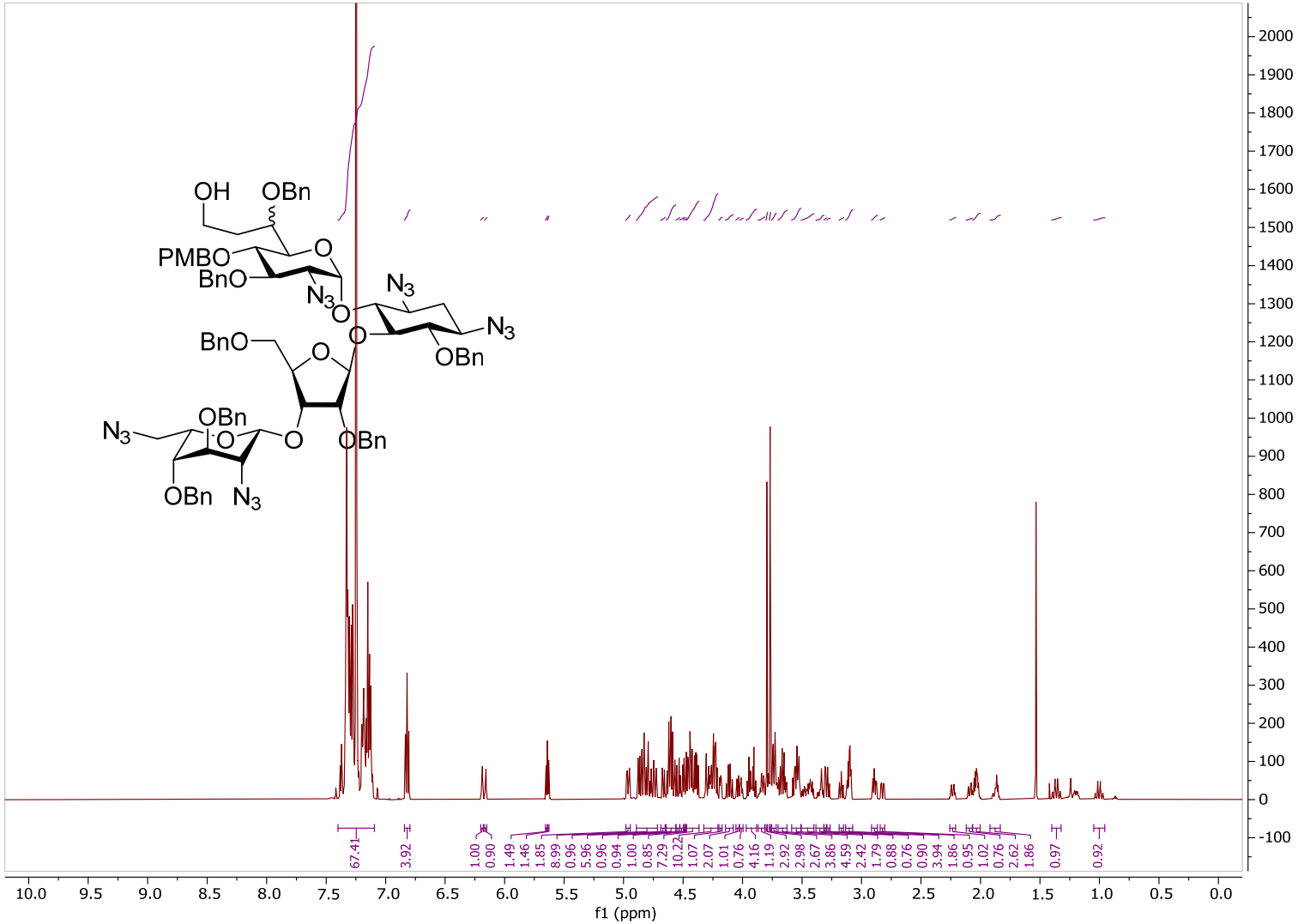
4-*O*-(2-Amino-4,9-anhydro-2,7,8-trideoxy-L-glycero-α-D-gluco-nonapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (8) HSQC



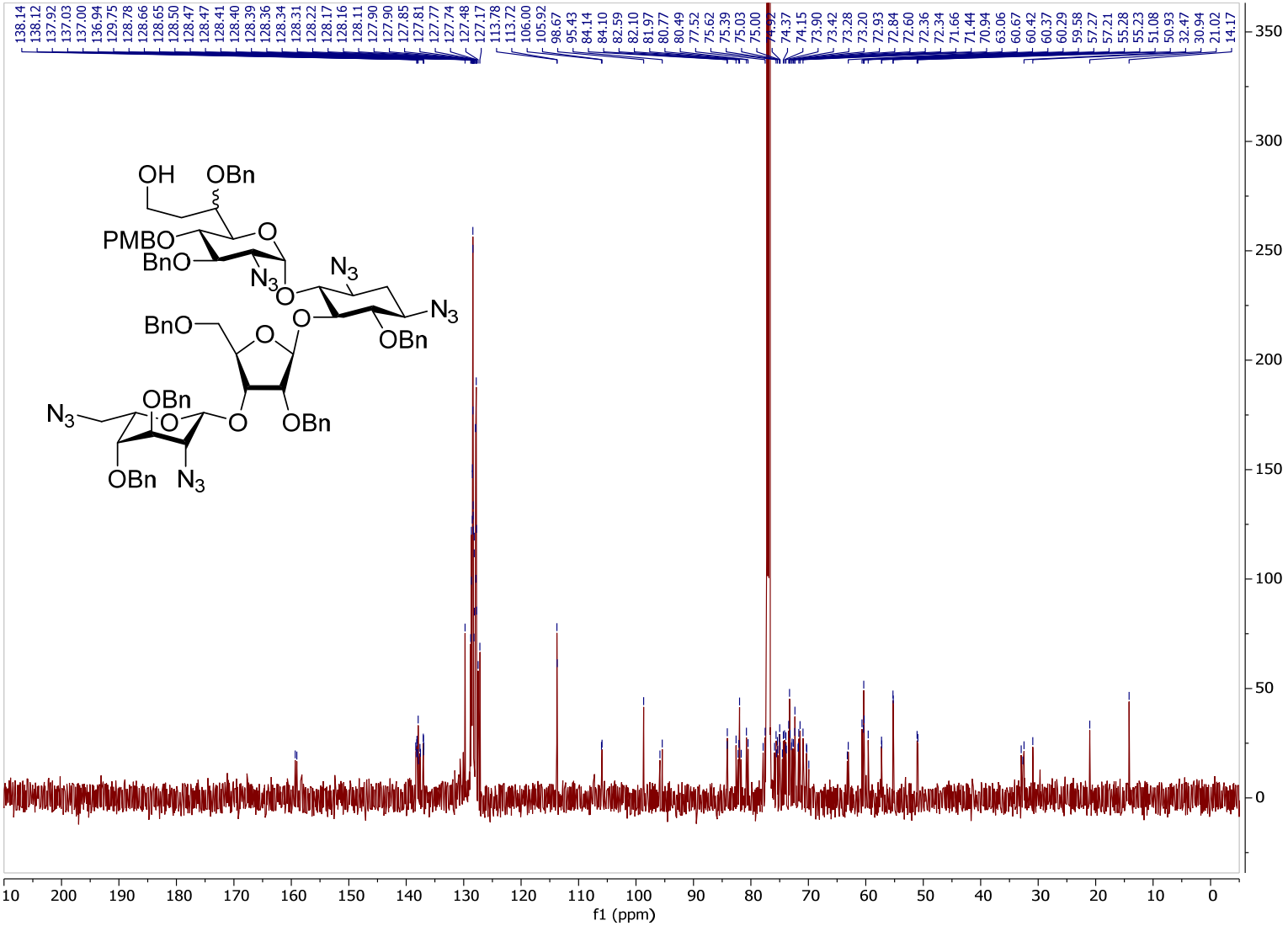
4-*O*-(2-Amino-4,9-anhydro-2,7,8-trideoxy-L-glycero-α-D-gluco-nonapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (8) HMBC



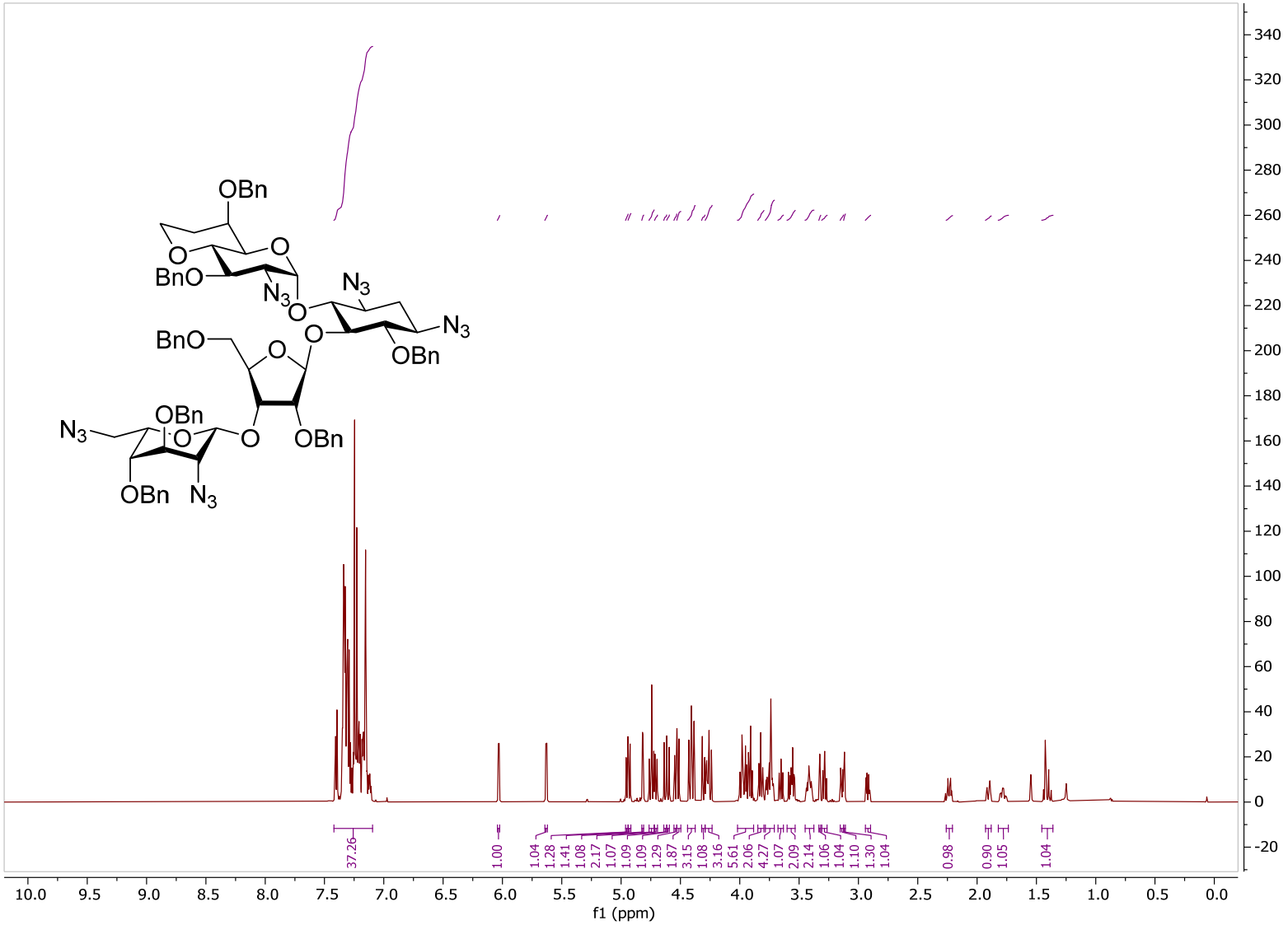
1,3,2',2''',6'''-Pentaazido-6,3',6',2'',5'',3''',4'''-hepta-*O*-benzyl-6'-*C*-(2-hydroxyethyl)-1,3,2',2''',6'''-pentadeaminoparomomycin (21) ^{1}H NMR (600 MHz, $CDCl_3$)



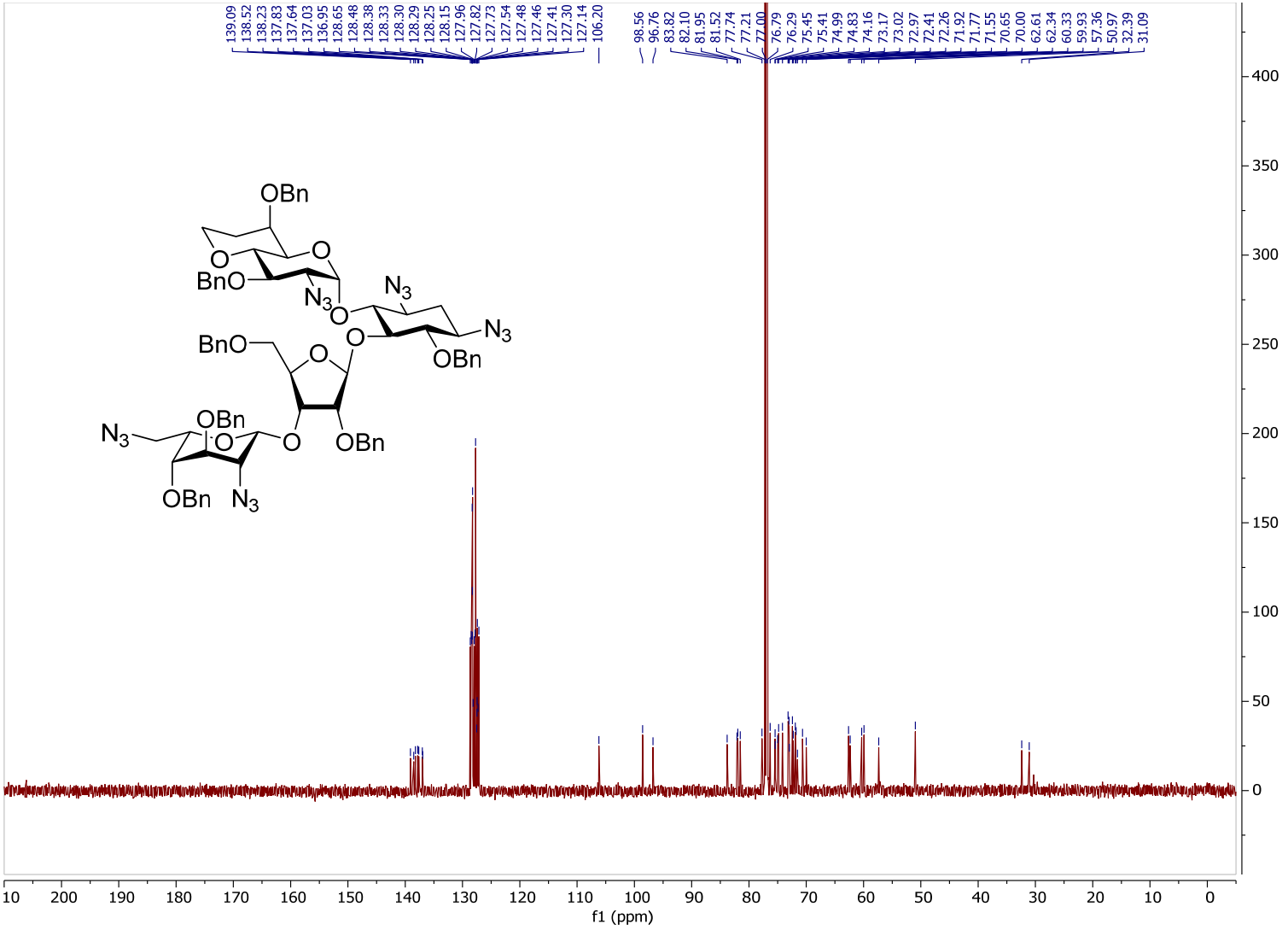
1,3,2’,2’’’,6’’’-Pentaazido-6,3’,6’,2’’,5’’,3’’’,4’’’-hepta-*O*-benzyl-6’-*C*-(2-hydroxyethyl)-1,3,2’,2’’’,6’’’-pentadeaminoparomomycin (21) ^{13}C NMR (151 MHz, $CDCl_3$)



4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,8-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (22(ax)) ^{1}H NMR (600 MHz, $CDCl_3$)



4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,8-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (22(ax)) ^{13}C NMR (151 MHz, $CDCl_3$)



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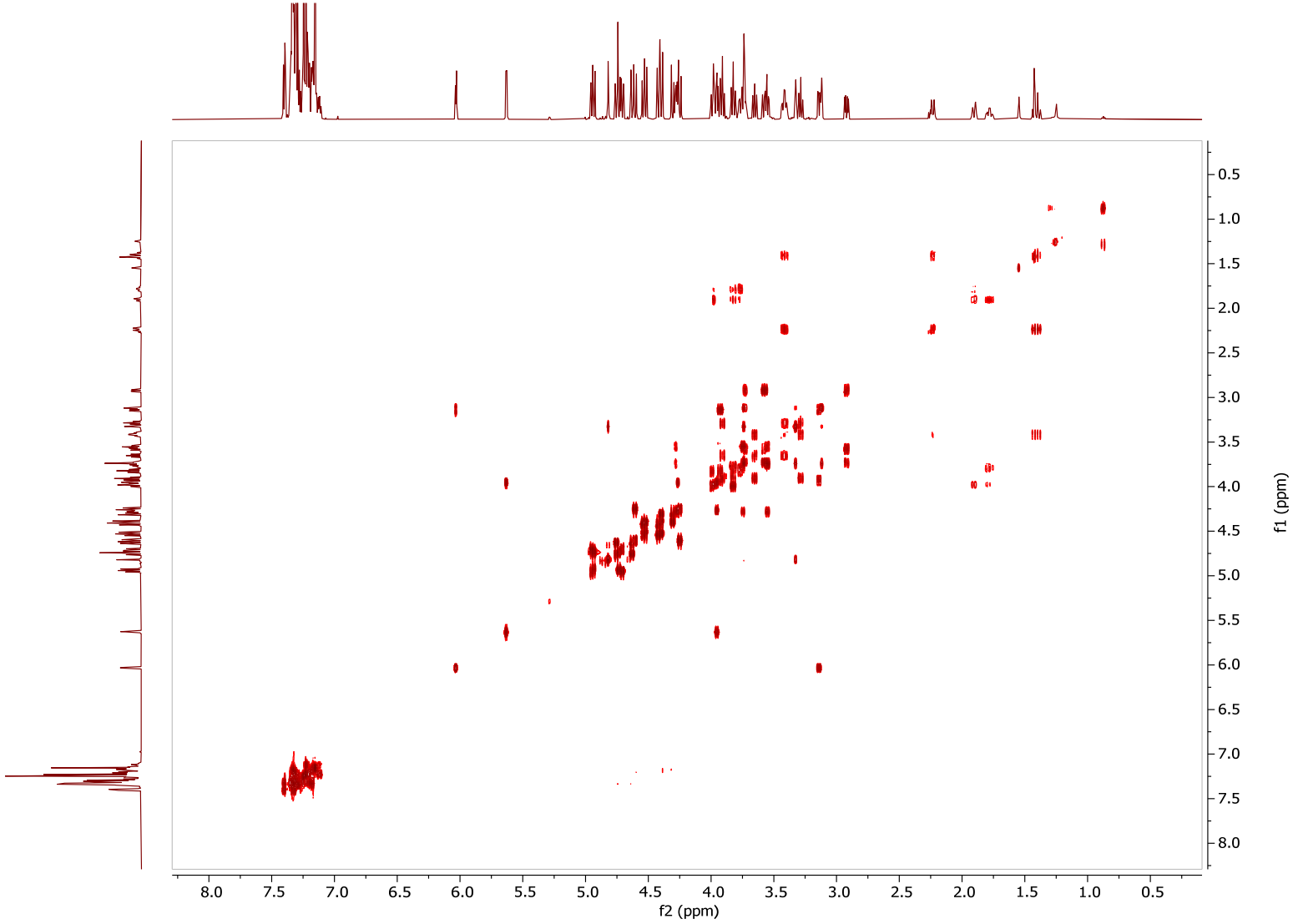

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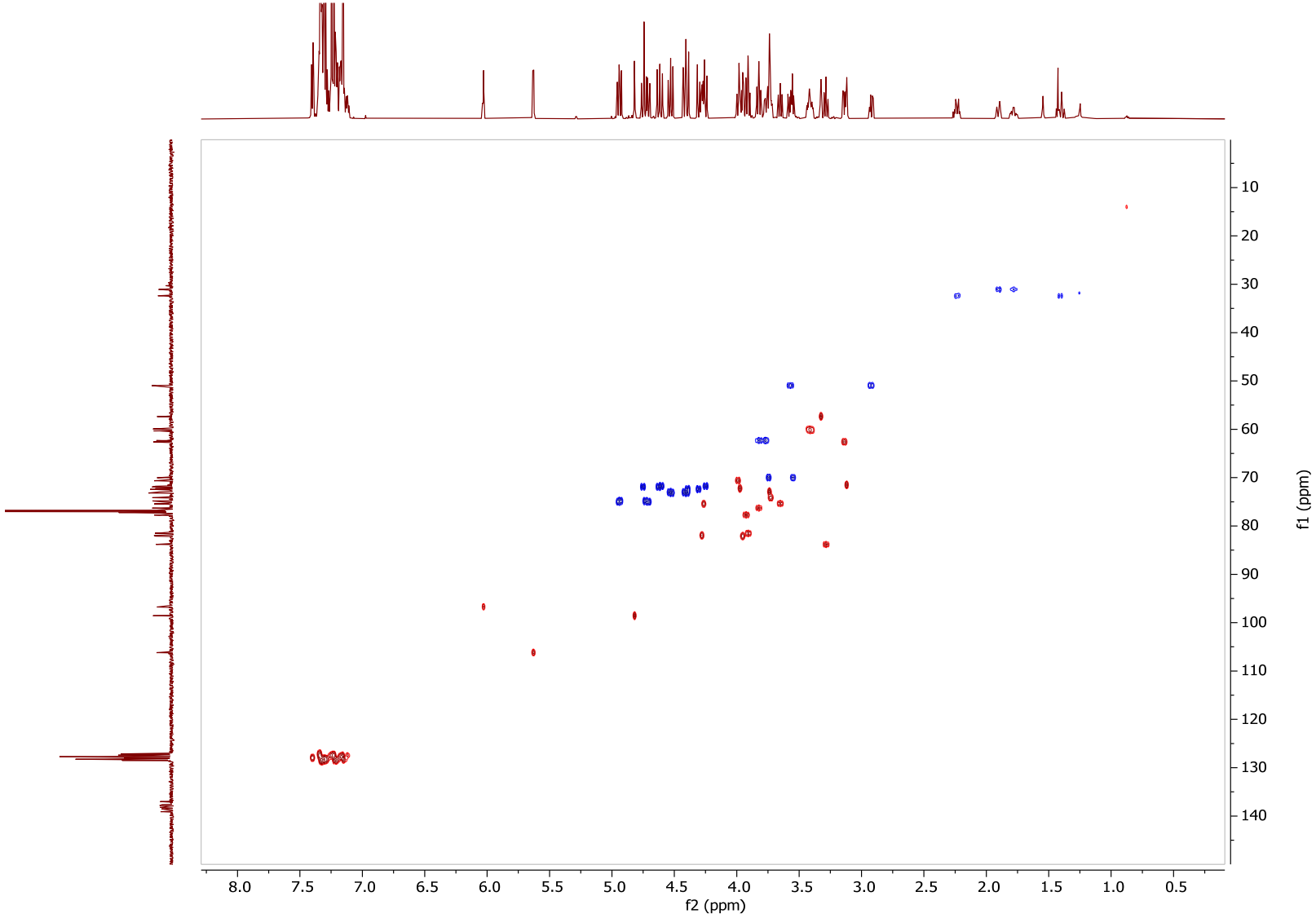

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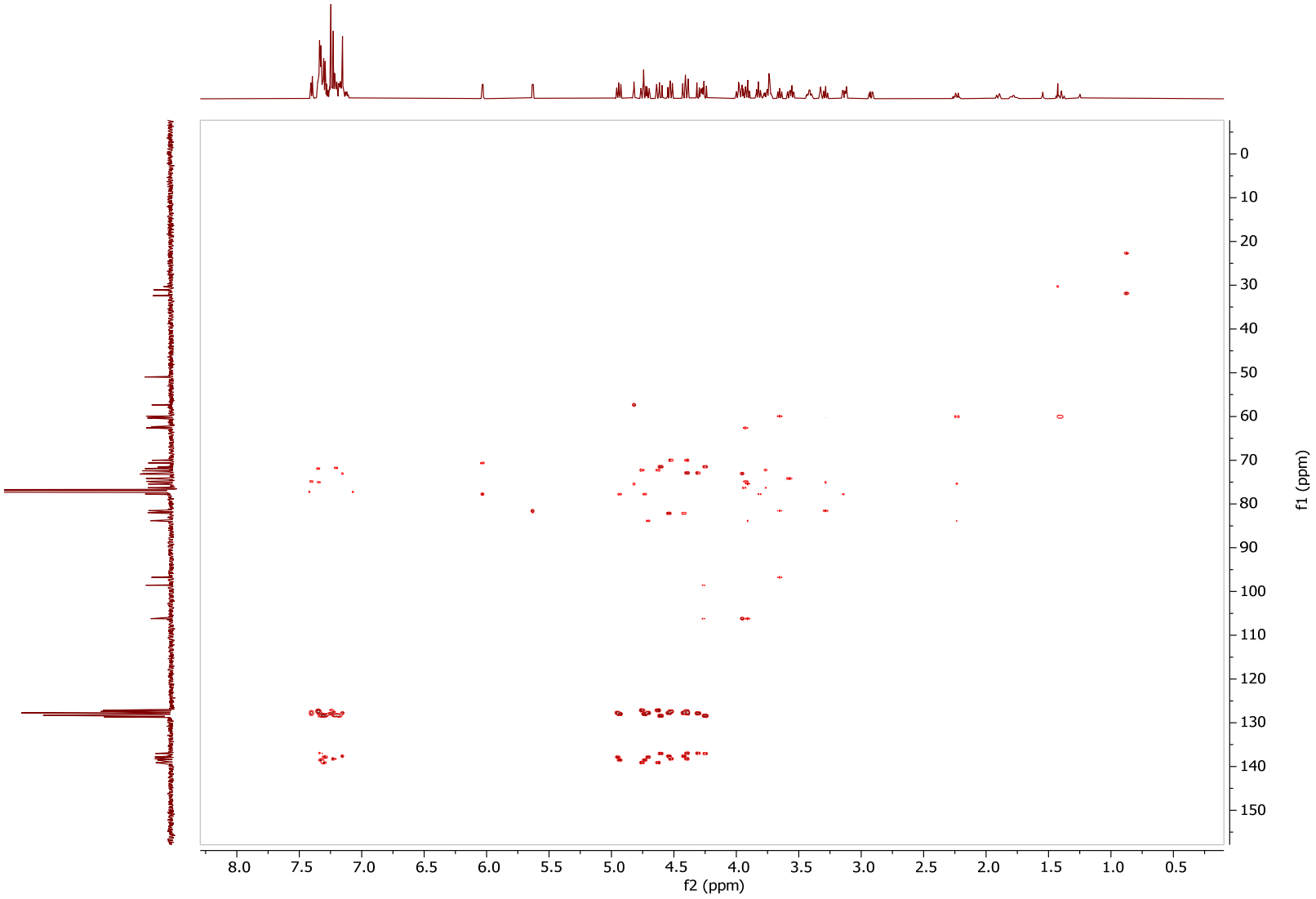

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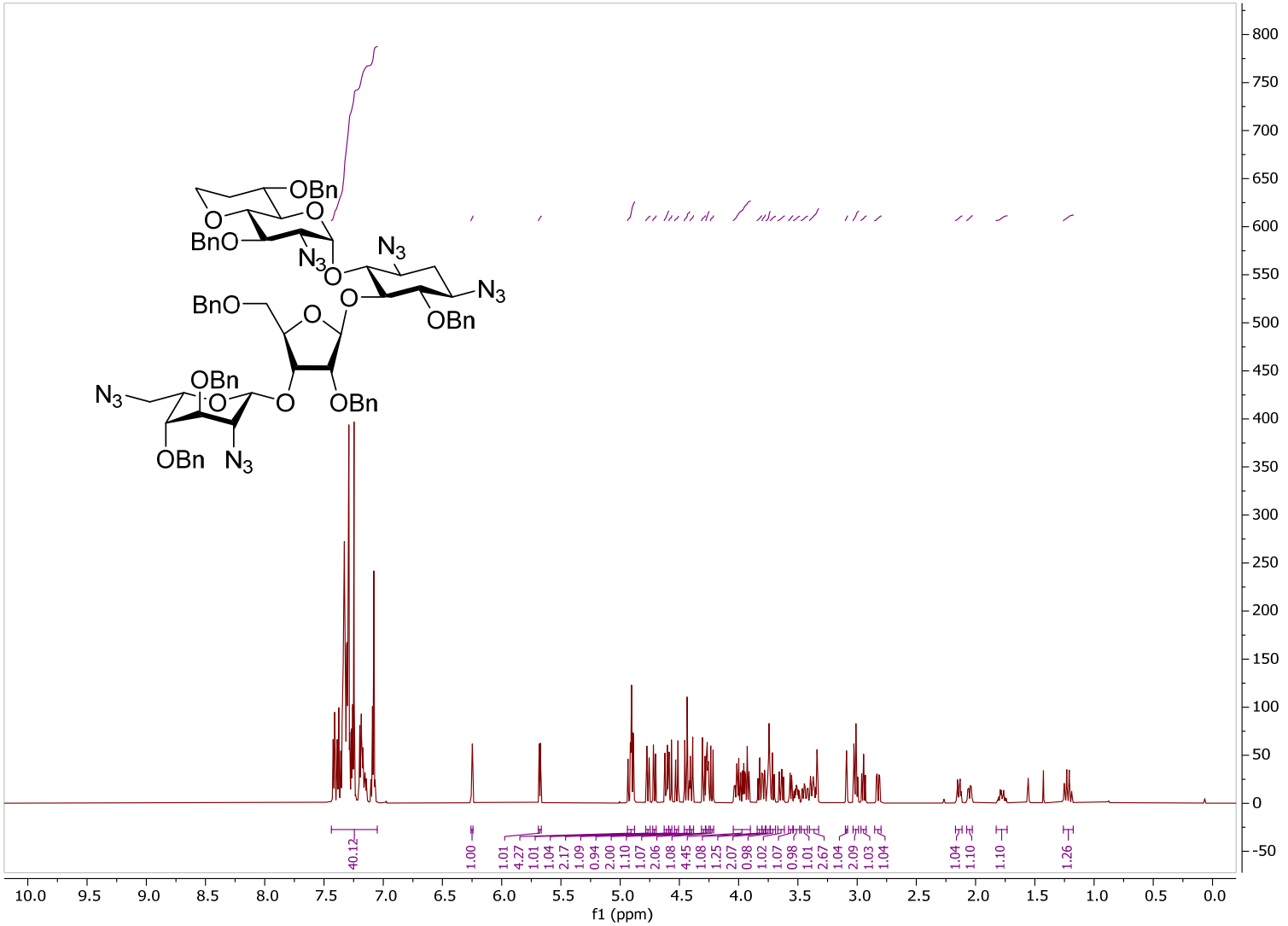
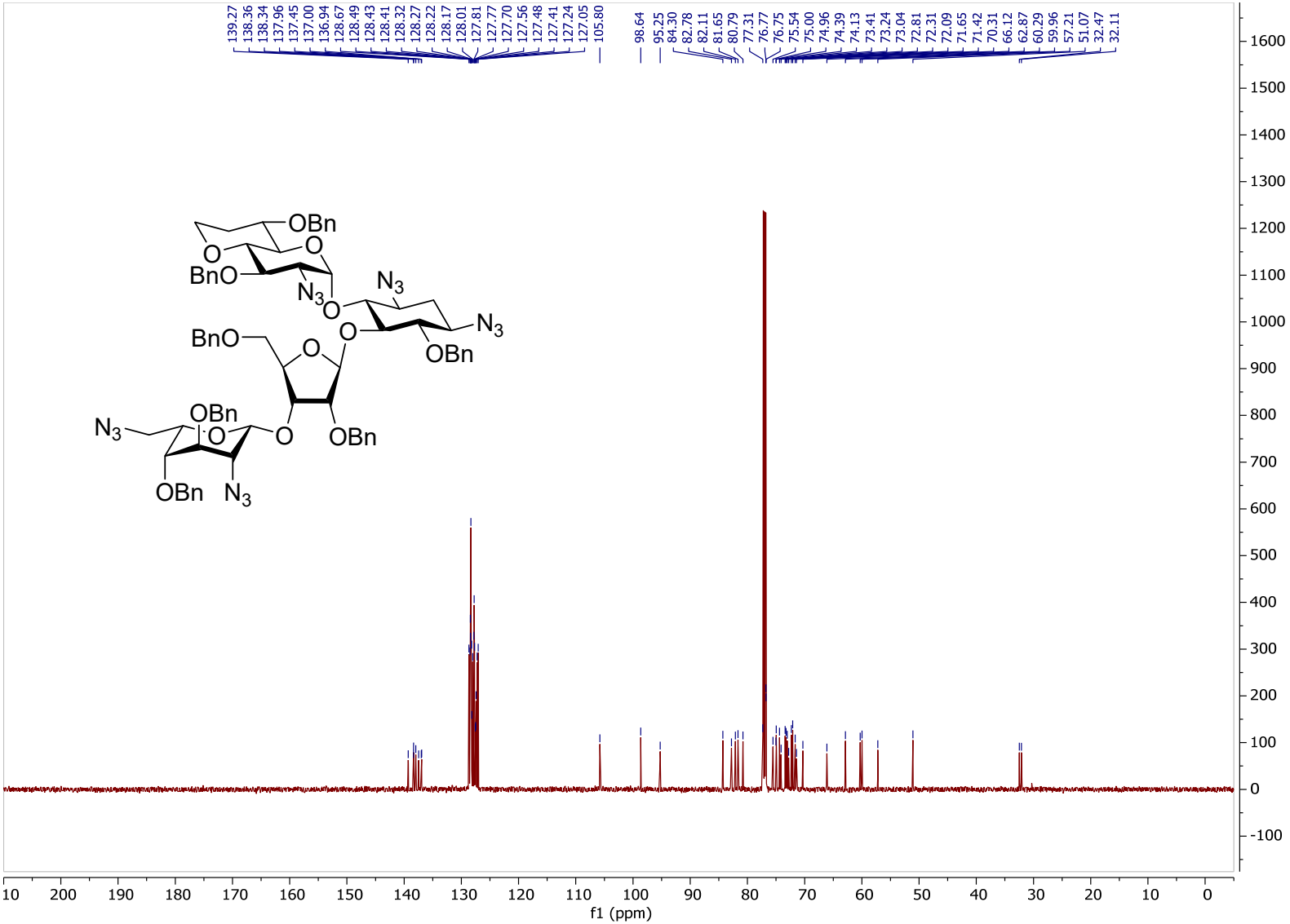
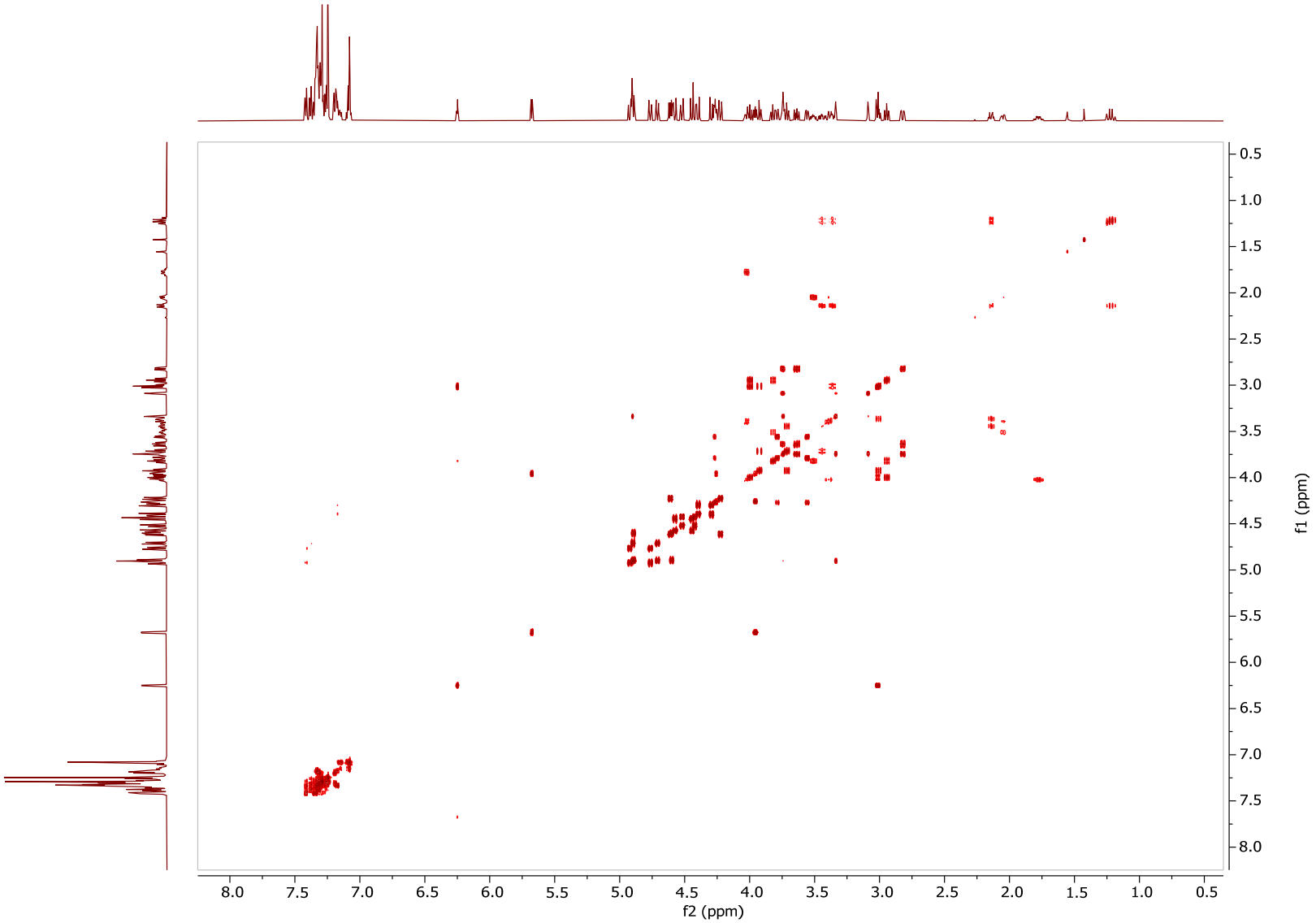


4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,8-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (22(eq)) ^{13}C NMR (151 MHz, $CDCl_3$)



4-*O*-(2-Azido-3,6-di-*O*-benzyl-4,8-anhydro-2,7-dideoxy-L-glycero-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diazido-3,4-di-*O*-benzyl-2,6-dideoxy-β-L-idopyranosyl)-2,5-di-*O*-benzyl-β-D-ribofuranosyl]-1,3-diazido-6-*O*-benzyl-2-deoxystreptamine (22(eq)) COSY



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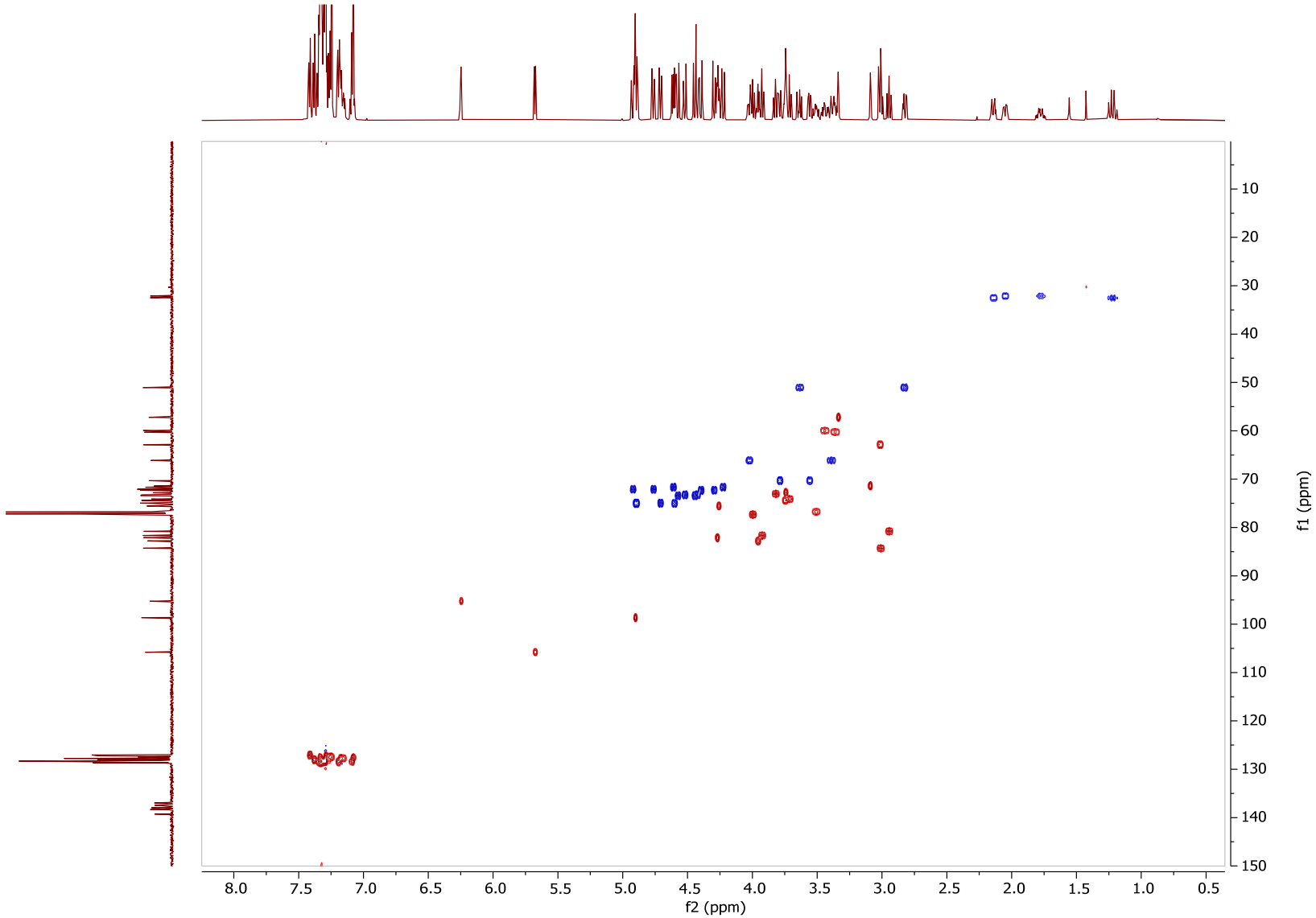

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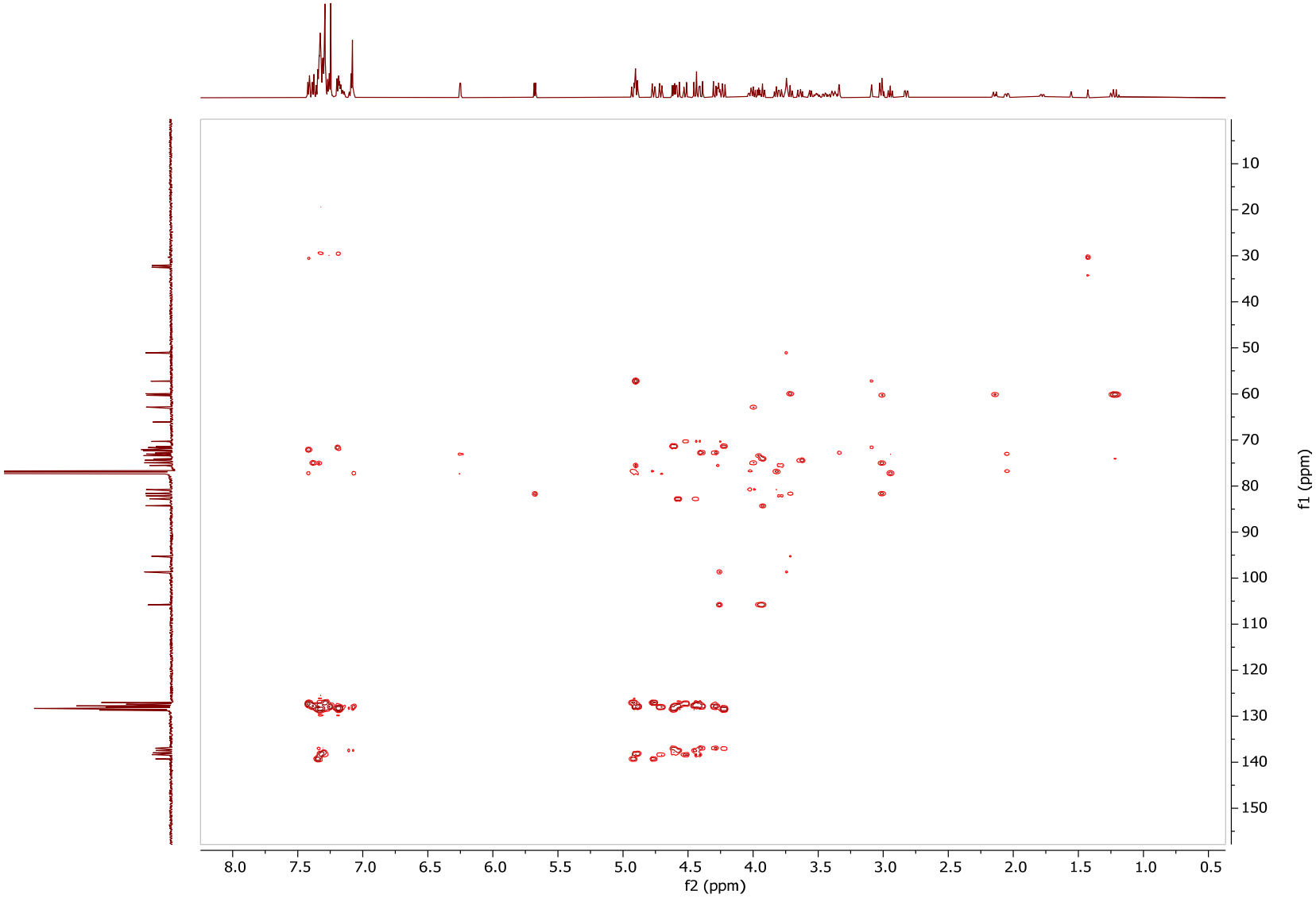
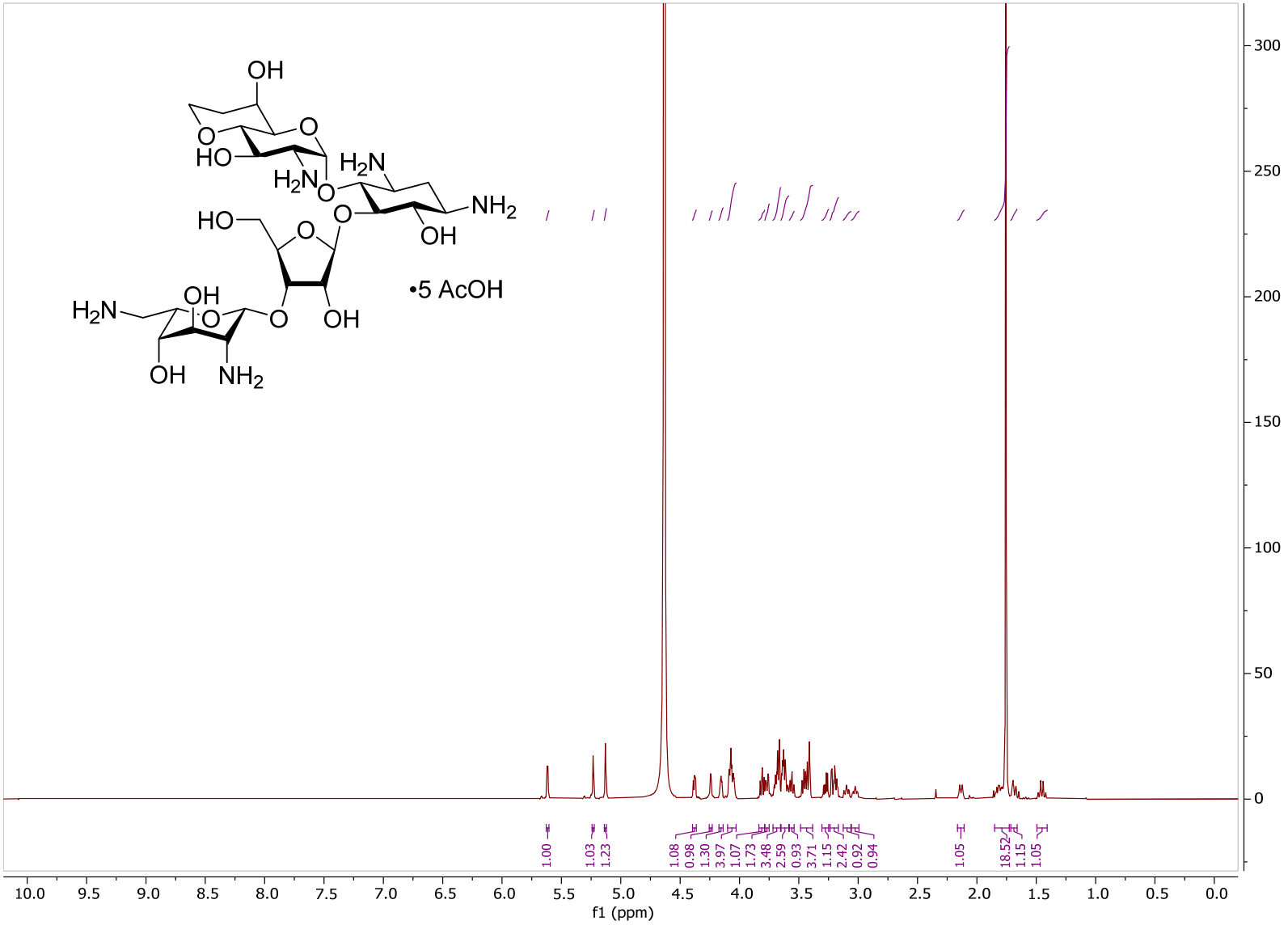


4-*O*-(2-Amino-4,8-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (11) ^{1}H NMR (600 MHz, D_2O)



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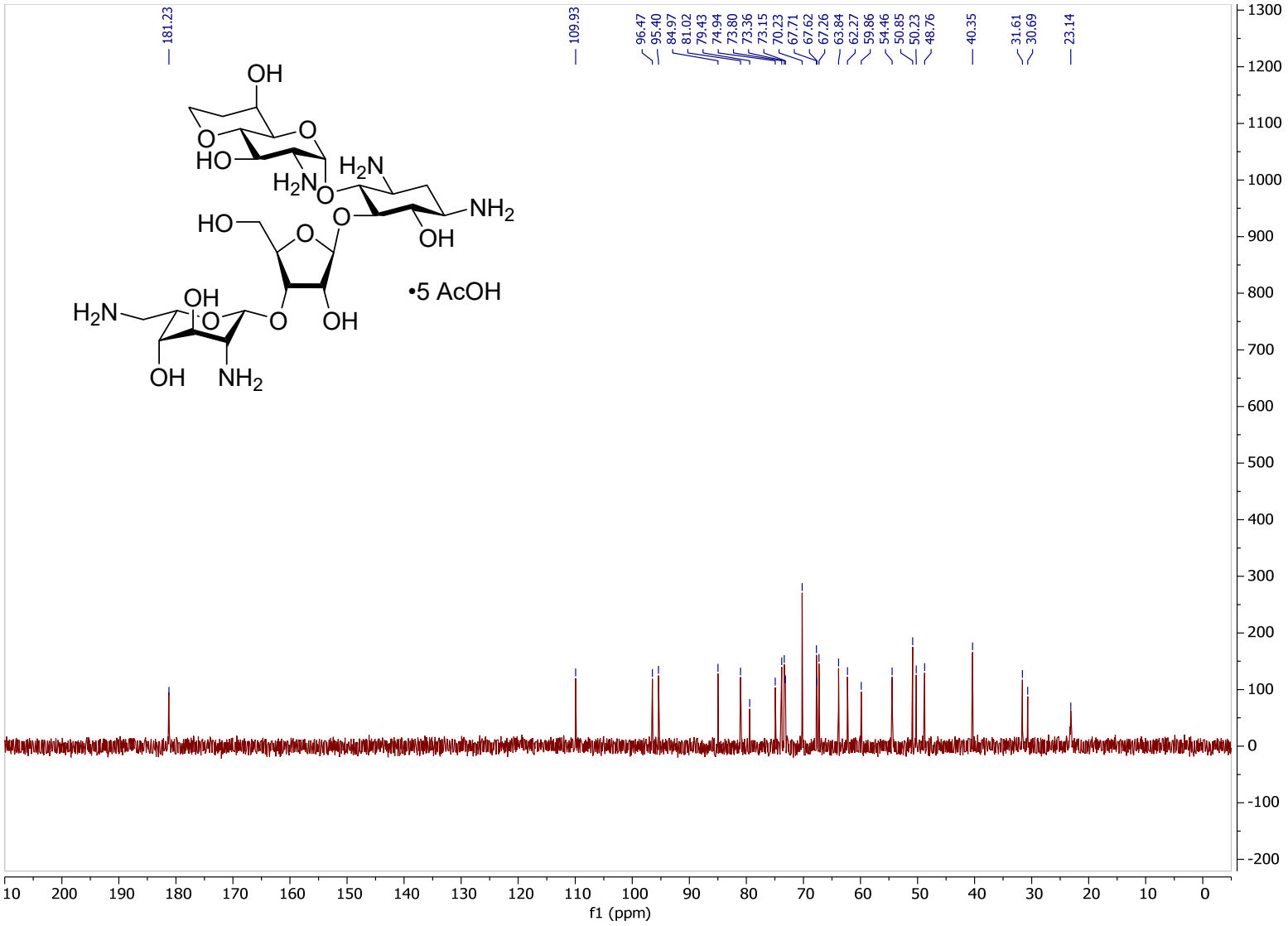
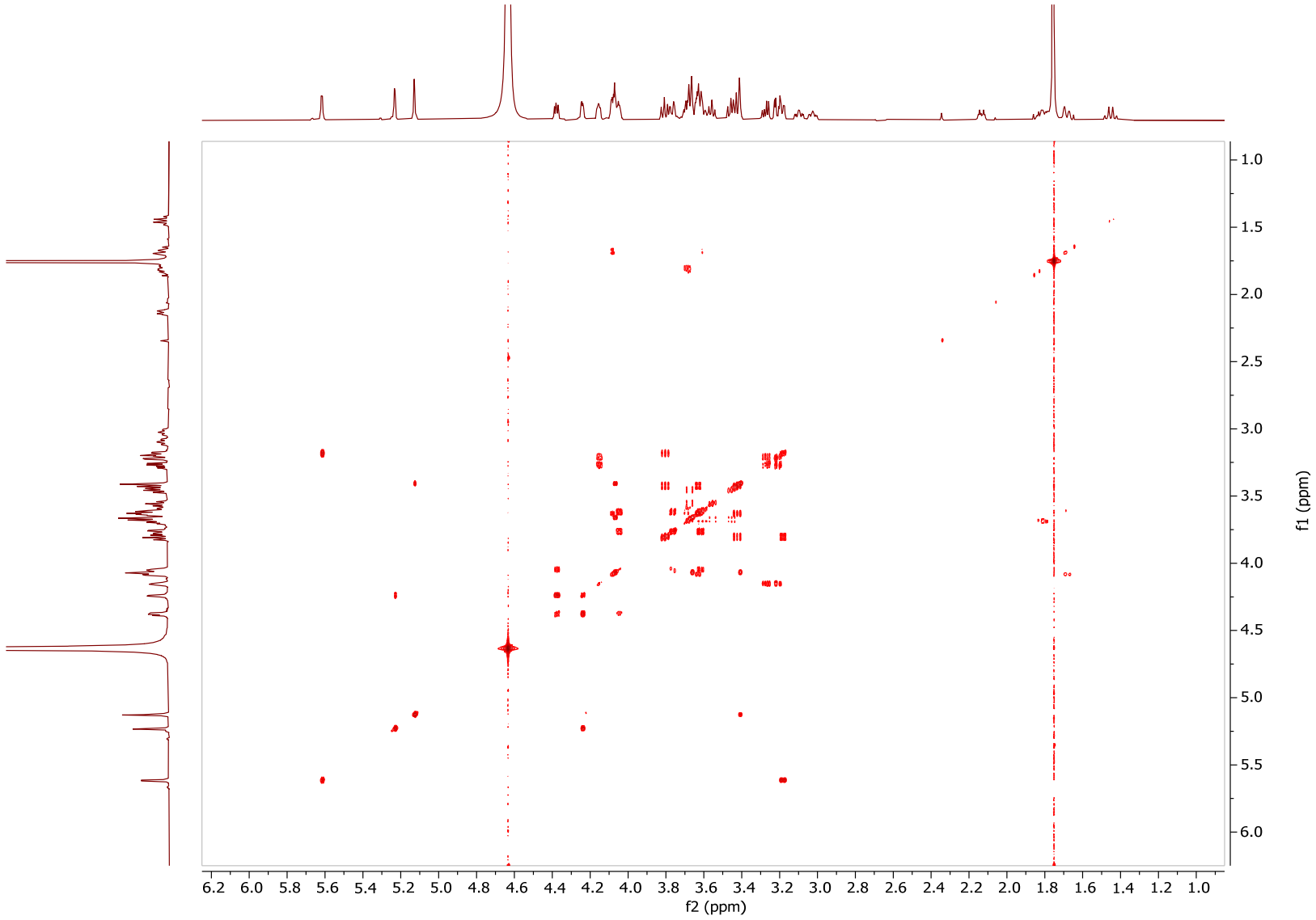


4-*O*-(2-Amino-4,8-anhydro-2,7-dideoxy-D-glycero-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (11) COSY



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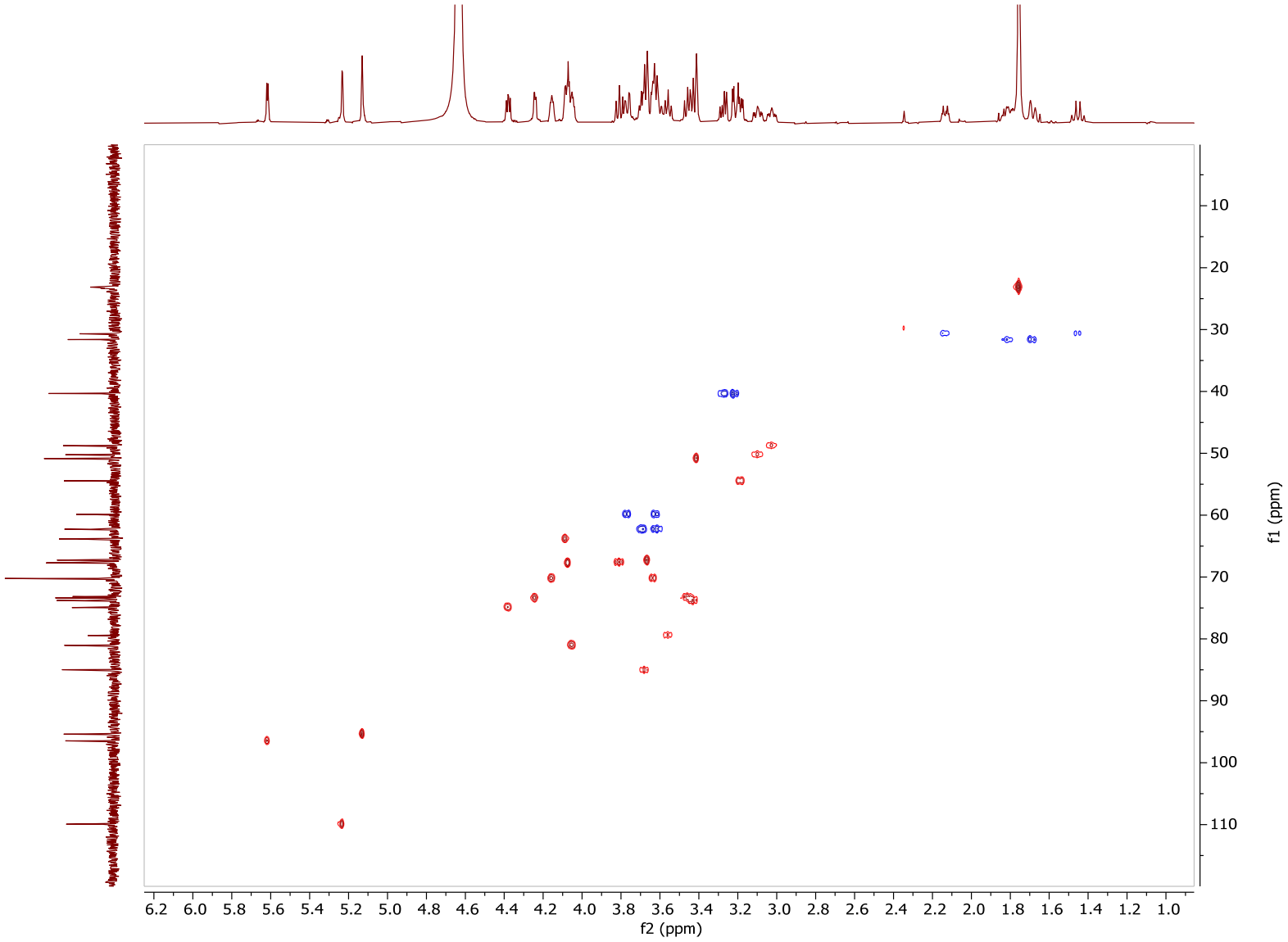

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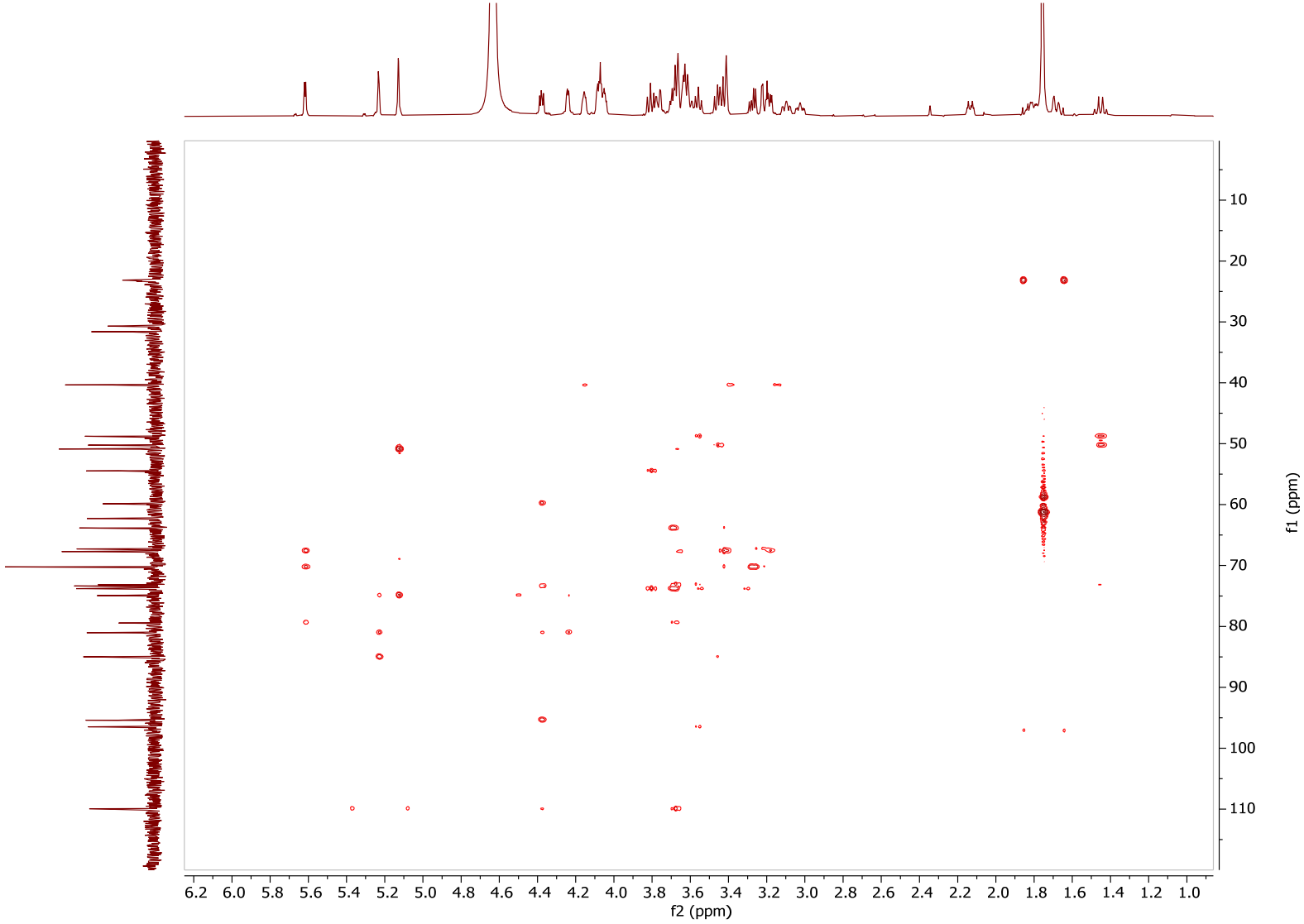

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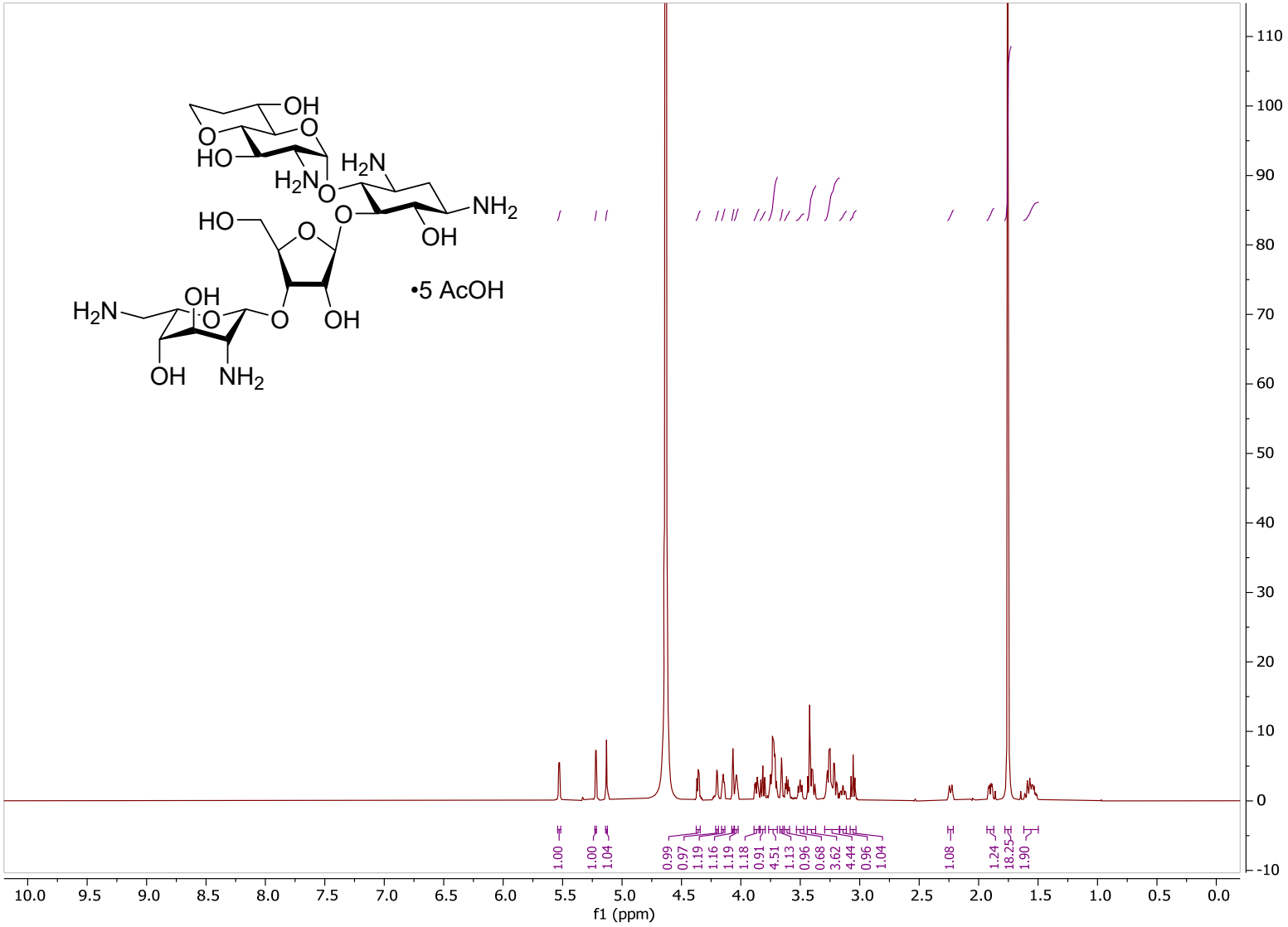
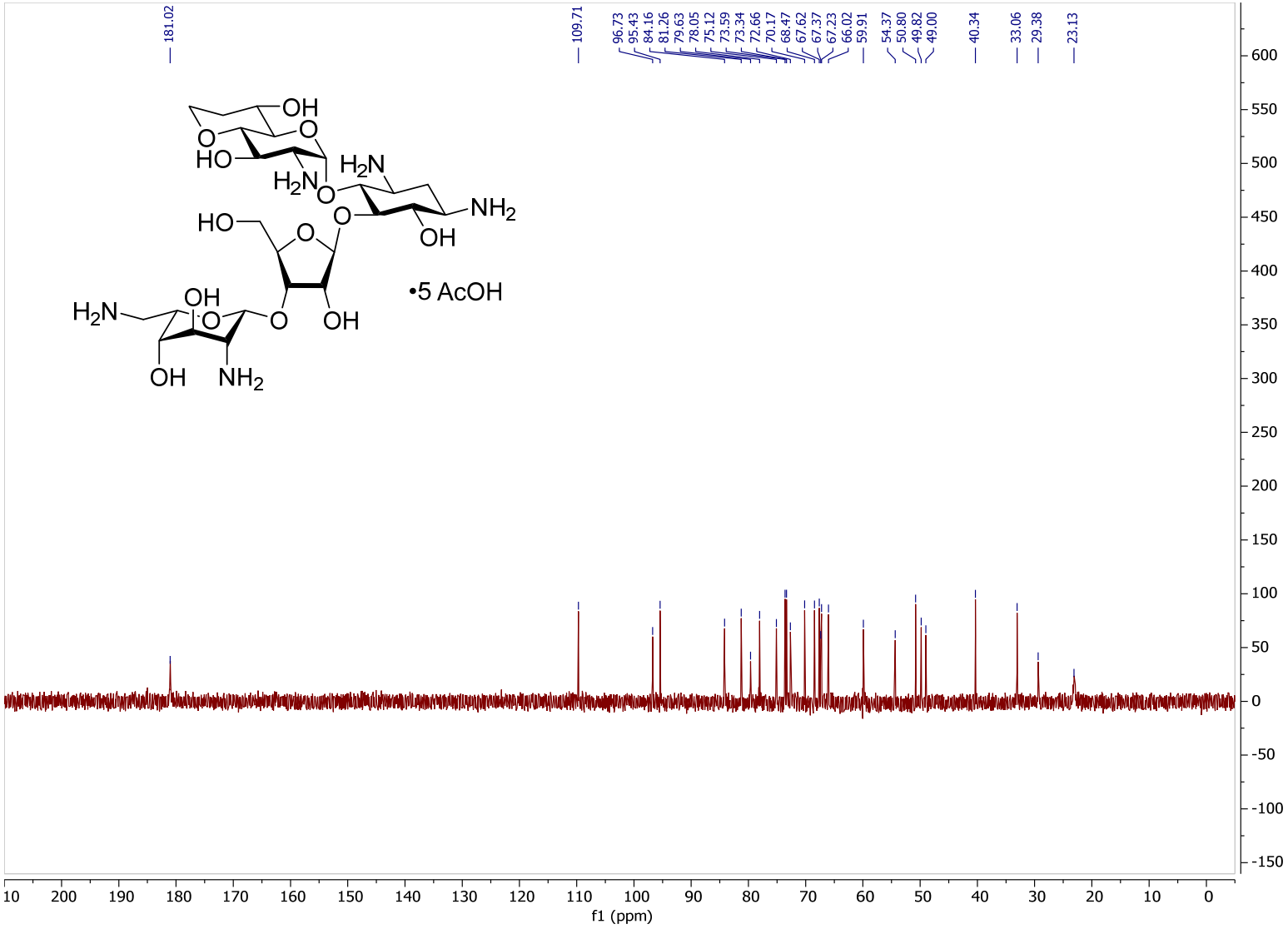


4-*O*-(2-Amino-4,8-anhydro-2,7-dideoxy-L-glycerol-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (10) ^{13}C NMR (151 MHz, D_2O)



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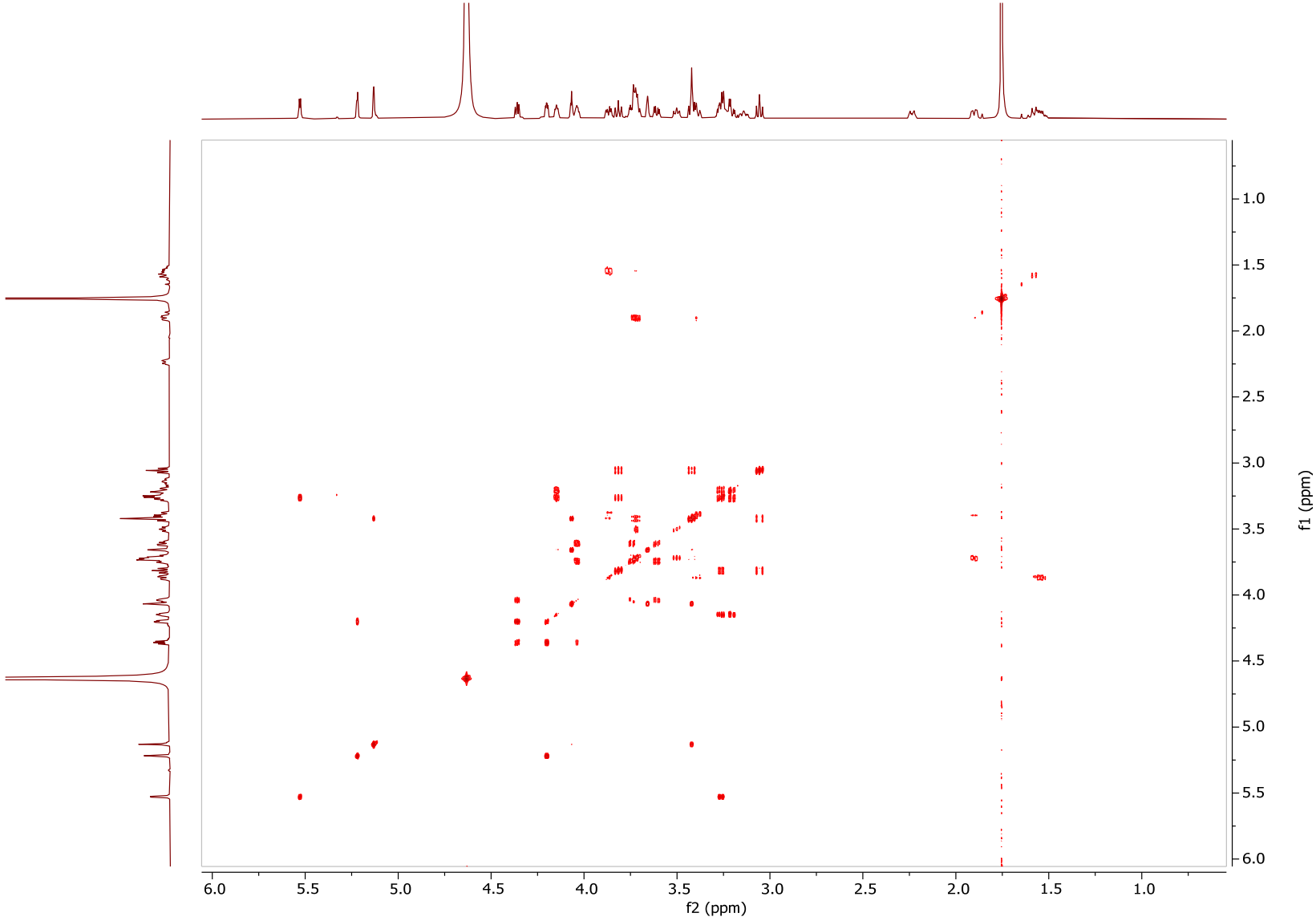
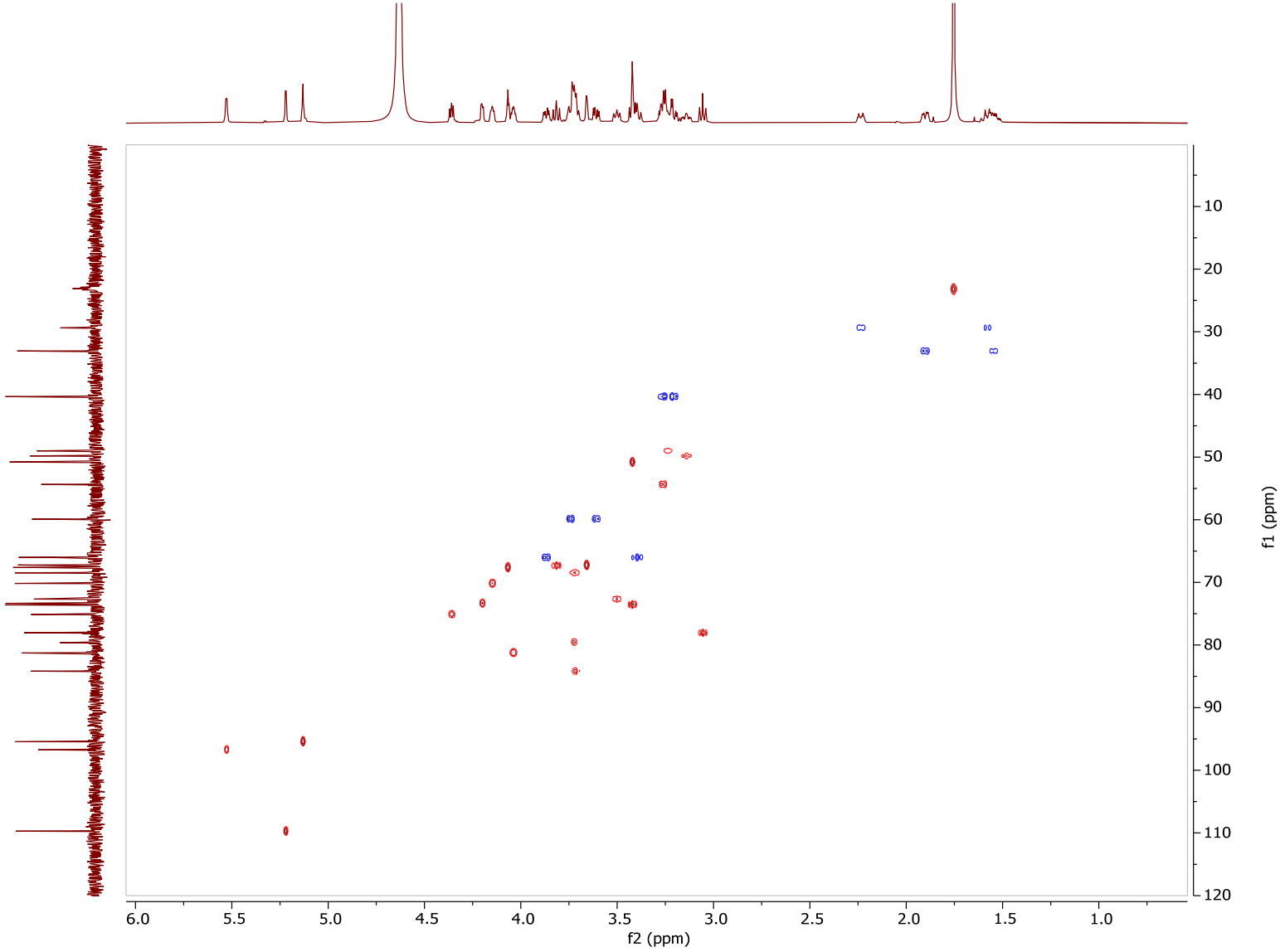


4-*O*-(2-Amino-4,8-anhydro-2,7-dideoxy-L-glycerol-α-D-gluco-octapyranosyl)-5-*O*-[3-*O*-(2,6-diamino-2,6-dideoxy-β-L-idopyranosyl)-β-D-ribofuranosyl]-2-deoxystreptamine pentaacetate salt (10) HSQC



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